DIRECTOR OF INDUSTRIES
Bengal

A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. IV.

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DIRECTOR OF INDUSTRIES
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BY

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim.	Annales de Chimie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik.	Annalen der Physik.
Ann. Physique	Annales de Physique.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth. Zeit.	Apotheker-Zeitung.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewer's Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr	Chemisches Zentralblatt.
Compt. rend	Comptes rendus hebdomadaires des séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedlander's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Met. & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmaceutische Zeitung.

Phil. Mag. . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . .	Philosophical Transactions of the Royal Society.
Phot. J. . . .	Photographic Journal.
Proc. Roy. Soc. .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie.
Zeitsch. angew. Chem	Zeitschrift fur angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift fur anorganische Chemie.
Zeitsch. Nahr. Genussm . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem . . .	Zeitschrift fur physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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L

L-ACID. 1-Naphthol-5-sulphonic acid.

LABDANUM or **LADANUM** *v.* OLEO-RESINS.

LABEL VARNISH *v.* VARNISH.

LABRADORITE *v.* FELSPAR.

LACCASE *v.* *Japanese Lacquer*, art. RESINS.

LAC DYE. Lac dye is produced by an insect, the *Coccus lacca* or *ficus*, living on the twigs of various kinds of trees, particularly the *Ficus religiosa* (Linn.), the *Zizyphus jujuba* (Lam.), and the *Butea frondosa* (Roxb.). These insects appear usually in November, and subsequently fasten themselves to the fleshy portions of the young branches. Gradually the abdomen of the insects becomes covered by a viscous fluid, which slowly forms a cellule surrounding the animal. The substance composing this cellule is the *stick lac*. The cellule attains its full size in March, and the insect then exhibits the appearance of a red oval-shaped, smoothly polished lifeless sac entirely filled with a beautiful red liquid; its size is then the same as that of the fully grown cochineal (Crookes, Dyeing and Calico Printing, 354). Commercial stick lac is chiefly gathered on the hilly banks of the Ganges in India, that for dyeing purposes possessing a deep red colour, whereas the pale perforated kind in which no insects exist is employed for varnish-making, and constitutes the material for *shellac*.

Of *lac*, the following varieties occur: *stick lac*, the crude product together with the twigs upon which it is formed; *grained lac*, the material removed from the twigs; and *caked lac*, the latter variety fused and cast into moulds.

Such a resinous material is not suitable for dyeing purposes, and a simple process is adopted to remove the colouring matter from the resin, or at least to obtain it in a more concentrated form. This consists in extracting the stick lac with hot dilute sodium carbonate solution, evaporating the extract, and moulding the residue into square cakes. According to Crookes the product, which is *lac dye*, contains on an average about 50 p.c. of colouring matter, 25 p.c. of resin, and 22 p.c. of earthy impurities.

Lac dye is an extremely ancient dyestuff, and was employed in the East for many centuries before it was known in Europe. It appears to have been introduced into this country about 1790. Early in the last century, lac dye was a very important article of commerce, so much so that at one time shellac was practically a bye-product of its manufacture. The position of these products has now been reversed, for whereas the dyestuff is almost no longer used, the shellac industry is of considerable importance.

According to the older writers, the colouring matter of lac dye was considered to be identical with that of cochineal, but that this is not the case has been clearly established by Schmidt (Ber. 20, 1285).

Laccaic acid.—Finely powdered lac dye, after treatment with dilute hydrochloric acid to remove mineral matter, is extracted with boiling water, and the colouring matter is precipitated from the resulting solution by means of lead acetate. The lead precipitate, suspended in water, is decomposed with sulphuretted hydrogen, and the filtrate which contains the free colouring matter is evaporated to dryness. The residue thus obtained is extracted with alcohol and ether and is then added to the solution until a precipitate no longer forms. The filtered liquid on gradual evaporation deposits crystals of laccaic acid. According to Schmidt, the amount of pure colouring matter which can be isolated by this method from a kilogram of lac dye is 20 grams.

A simpler process has been described by Dimroth and Goldschmidt (Annalen, 1913, 399, 62), in which the stick lac is digested in water at 50°, the clear red solution, after cooling, acidified with acetic acid, separated from the resinous matter that is precipitated, and, after evaporation to small bulk, acidified with hydrochloric acid. When the crude product thus obtained is crystallised from hot 85 p.c. formic acid, washed, dried (at 60°–70°C.), and recrystallised from hot dilute hydrochloric acid, laccaic acid separates in the form of dark red microscopic rhombohedra. The acid is soluble in water yielding blood-red solutions, but is insoluble in ether; when heated it decomposes at about 180°, yielding a small quantity of a red sublimate. Only the sodium hydrogen salt has been prepared in crystalline condition, and to this Dimroth ascribes the formula

$$C_{20}H_{12}O_{10}Na_2.C_{20}H_{13}O_{10}Na$$

whilst he concludes that the acid has the composition $C_{20}H_{14}O_{10}$, and not $C_{16}H_{12}O_8$, as previously supposed.

Although no distinction is to be observed in the absorption spectra of the aqueous and alkaline solutions of laccaic and carminic acids, it is possible when the colouring matters are dissolved in sulphuric acid to discriminate between them in this way. When fused with potassium hydroxide, laccaic acid gives, in addition to a substance (*a*) volatile in steam, colourless needles, m.p. 142°–143°; a compound (*b*) $C_{10}H_6O_6$, or $C_{10}H_8O_6$, m.p. 285°, readily soluble in water; a compound (*c*) $C_8H_8O_3$, m.p. 169°, possibly a hydroxytoluic acid; and (*d*) an easily soluble substance, the aqueous solution of which gives a black coloration with ferric chloride (Schmidt).

Reduction of laccaic acid with tin and hydrochloric acid, or with zinc-dust and aqueous ammonia, yields a compound $C_{20}H_{16}O_9$, which crystallises in brown-yellow rhombohedra, and which on oxidation by means of cupric chloride and hydrochloric acid, yields a substance of the composition $C_{20}H_{14}O_9$, which Dimroth considers is related to the former substance as quinone to hydroquinone.

Although laccaic acid does not yield crystalline bromination products similar to α- and β-bromocarmine, compounds of this nature have been obtained by Dimroth from its oxidation product, calaic acid.

Calaic acid is produced when laccaic acid is oxidised by means of hydrogen peroxide (2½–3 molecular proportions) in the presence of a catalyst (cobalt, manganous, cerous, or ferrous salts; manganous chloride is best). This acid, $C_{18}H_{14}O_{11}$, crystallises from ether in small yellow prisms, and from water in needles having the composition $C_{18}H_{14}O_{11}, 2\frac{1}{2}H_2O$. It does not possess dyeing properties, contains one carbonyl and three carboxyl groups, and may be purified by means of its crystalline barium salt. A silver salt, $C_{18}H_{12}O_{11}Ag_2$, has also been prepared.

When calaic acid is brominated in glacial acetic acid, two products are formed: (i) an α-ketonic acid $C_{12}H_{10}O_6Br_2$, and (ii) β-bromolaccain $C_{12}H_5O_8Br$, these products being separated by taking advantage of the solubility of the latter in cold acetone.

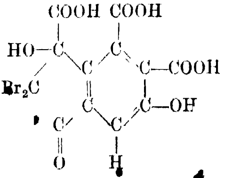
The α-ketonic acid forms brown-yellow crystals, m.p. 208°–209°; it gives an impure red-violet colour reaction with ferric chloride, and when heated to 80°–90° with concentrated sulphuric acid, it loses carbon monoxide, yielding a monobasic acid $C_{11}H_{10}O_5Br_2$, which has m.p. 245°–246° (decomposition), and gives an intense violet colour reaction with ferric chloride. The keto-acid forms a phenylhydrazone and semicarbazone, and, by treatment with methyl alcoholic hydrobromic acid, yields the hydrobromic acid compound of its methyl ester $C_{13}H_{12}O_6Br_2.HBr$, colourless needles, m.p. 133°–134° (decomposition).

β-Bromolaccain separates from water in crystals of the composition

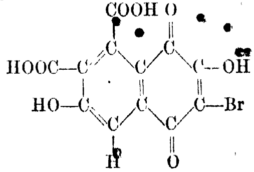
$$C_{12}H_5O_8Br, 2H_2O$$

it has m.p. 234°–235° (decomposition). It dyes wool orange from an acid bath, and gives a strong red colour with ferric chloride. The potassium salt $C_{12}HO_8BrK_4, H_2O$, crystallises in hexagonal plates. Concentrated sulphuric acid and acetic anhydride produce *diacetyl-β-bromolaccain anhydride* $C_{16}H_7O_9Br$, indicating that two hydroxy groups are present in the molecule, and that it also contains two carboxyl groups in the ortho position.

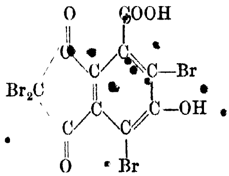
Oxidation of β-bromolaccain by means of hydrogen peroxide in warm glacial acetic acid yields two products, viz. (i) *hydroxy-tricarboxyphenyl-glyoxylic acid*, and (ii) a compound $C_{12}H_6O_9Br_2$. The former, which is the chief product, crystallises in plates, m.p. 229·5°–230° (decomposition), and on treatment with concentrated sulphuric acid at 130°–140° yields a phenol-tetracarboxylic acid which melts at 212°–214° (decomposition). The second oxidation product of β-bromolaccain has m.p. 188°–190° (decomposition), and readily loses bromine: for it Dimroth tentatively proposes the formula—



For β-bromolaccain itself Dimroth and Goldschmidt suggest the structure—



and for this they find support in the fact that it resembles 2 : 6-dihydroxy-α-naphthoquinone in its colour reactions. Moreover, it behaves very similarly to β bromocarmine in that it yields an indone derivative, *α-bromolaccain* (*cf.* α-bromocarmine), when its boiling solution in water is treated with bromine :—



This compound crystallises in colourless needles, and yields 2 : 6-dibromophenol-3 : 4 : 5-tricarboxylic acid, m.p. 257°–258°, and bromoform when treated with sodium hypobromite.

Dyeing properties.—The dyeing properties of lac dye are practically identical with those of cochineal, but the shades obtained are somewhat faster. Owing to the resinous and mineral impurities accompanying the colouring matter, it is not readily soluble in water, and before use it is therefore ground to a paste with the requisite quantity of tin spirit together with a little hydrochloric acid, and allowed to stand overnight. Cochineal and lac dye can be used together with advantage, or after the wool is dyed with lac it may be entered into a fresh bath with cochineal. Its employment at the present time is, however, extremely limited.

Fowler (Indian Textile Jour. 1917, 244) has made attempts to standardise various Indian colouring matters so that they may be marketed in uniform strengths. It would appear that 'Lac dye' is one of those with which he has been concerned. A. G. P.

LACMOID $C_{12}H_9NO_4$ (?)

Preparation.—(1) A mixture of resorcinol (20 parts), sodium nitrite (1 part), and water (1 part) is slowly heated to 110°, when a vigorous reaction sets in; the mass is then kept at 115°–120° until it has become quite blue and no more ammonia is evolved. The product is dissolved in water and the lacmoid precipitated with hydrochloric acid (Traub and Hock, Ber. 1884, 17, 2615). (2) By fusing resorcinol (5 parts) with potassium nitrite (6 parts) (Benedict and Julius, Monatsh. 1884, 5, 534). (3) By the action of H_2O_2 on ammoniacal resorcinol solution (Wurster, Ber. 1887, 20, 2938).

To purify the substance, extract it almost completely with boiling water, cool, filter, and acidify the blue solution with hydrochloric acid. Filter off the precipitated lacmoid, wash with cold water and dry it below 100°. An alternative method is to warm gently powdered lacmoid (8 parts) with 20 p.c. alcohol (100 parts) for 15 minutes, cool and filter (Foerster, Zeitsch. angew. Chem. 1890, 3, 163).

Properties.—A glistening brown powder, easily soluble in methyl, ethyl, or amyl alcohol, acetone, acetic acid, or phenol, less easily in ether or water, insoluble in benzene or petroleum spirit. It dissolves in concentrated HCl or H_2SO_4, yielding a blue solution. Heated below 200° it decomposes.

Lacmoid differs from the colouring matter of litmus in being soluble in strong alcohol. Its absorption spectrum resembles that of azolitmin (Hartley, Proc. Roy. Dublin Soc. 5, 159).

For the use of lacmoid as an indicator, *v.* Thomson (Chem. News, 1885, 52, 18, 29) and ACIDIMETRY AND ALKALIMETRY.

LACQUER (*Urushi, Ki-urushi*). A varnish usually obtained from the juice of *Rhus vernicifera* (DC.), a tree indigenous to China, whence in early times it was introduced into Japan (Bull. Imp. Inst. 1910, 8, 32; J. Soc. Chem. Ind. 1910, 639).

Burmese lacquer, or 'thitsi,' is obtained from the stems of *Melanorrhoea usitata* (Wall) as a grey viscous liquid of sp.gr. 1·0016 at 20°, which, on exposure to air, becomes first brown, and then, very rapidly, deep black. The drying of the lacquer is not accelerated by siccatives, and is retarded by dry heat, the presence of moisture being essential. The constituent of the lacquer soluble in alcohol is not identical with the urushinic acid (urushiol) of Japan lacquer. It is known as *thitsiol* $C_{23}H_{36}O_2$, and is a homologue of *iso*hydrourushiol. The ether extract consists of a gummy substance soluble in water, and a nitrogenous, coagulable substance which acts as an oxygen carrier in the drying of the lacquer, but loses its activity when heated above 60° (Rosenthal, Farbenzeit., 1914, 19, 1573; Majima, Ber. 1922, 55, 191).

Chinese lacquer. The tree is abundant in Central China, growing wild or under cultivation at altitudes of 3000 to 7500 feet. It is tapped in June or early July; shallow incisions are made in the bark of the stem and the greyish-white, milky juice collected in shells, bamboos, &c., and covered with oiled paper to prevent oxidation. The tapping is repeated seven times at intervals of 7 days, and the tree is then left for 5–7 years to recover. Much of the varnish is sent to Japan. The lacquer is frequently adulterated with tung oil.

Japanese lacquer. The lacquer tree grows abundantly all over Japan, and is cultivated largely in the district north of Tokyo. Tapping takes place when the tree is 10 years old and is continued from June to October, each tree yielding from 27 to 54 grams of lacquer. Usually the tree is left to recover, but sometimes it is cut down. In the latter case, a further yield of lacquer is obtained from the branches by steeping them in water for 10–20 days, and then making incisions and heating the water to cause the sap to exude. The varnish thus obtained, called *seshine-urushi*, is harder and of poorer quality, and is used only for groundwork and for cheap articles. The best quality is obtained from between the inner and outer bark of trees from 14 to 15 years old. It is called *ki-urushi* (Pudor, Zeitsch. öffentl. Chem. 1910, 16, 315). A very inferior quality, known as *Moku-yshi*, is used mixed with the better kinds in varying proportions. Both Chinese and Japanese lacquer contain urushiol (*q.v.*).

Yunan lacquer is derived from *R. succedanea* (L. fils), Formosan lacquer from *Semeocarpus vernicifera*, and ivy lacquer from *R. toxicodendron*. These contain *laccol* $C_{23}H_{36}O_2$, a homologue of urushiol. Siam lacquer is probably a mixture of Yunan and Burmese lacquers. Korean lacquer is probably identical with Japanese lacquer (Riko Majima, J. Tokyo Chem. Soc. 1919, 40, 91).

The raw varnish is packed in wooden tubs and covered with oiled paper to prevent oxidation. It is prepared for use by various processes, the quality and value of the varnish and of the lacquered ware produced depending upon the time and care spent upon the purification.

The juice is strained from particles of bark, &c., and is allowed to stand in wooden vessels until it separates into various layers, when the lighter and finer qualities are decanted from the heavier and inferior varnish. The product is finally filtered through hempen or cotton cloth and exposed in shallow wooden pans to the heat of the sun or to artificial warmth. It thus becomes syrupy and of a dark brown colour, the change being due principally to loss of water. It is thinned with camphor or oil of turpentine or other suitable solvent.

Coloured lacquers are prepared from *ki-urushi* during the exposure to the sun (*v.s.*) by mixing in appropriate pigments, those most commonly employed being as follows (Miyama, J. Coll. Engineering, Imp. Univ. Tokyo, 1908, 4, 201; J. Soc. Chem. Ind. 1909, 318):—

White.—Barium sulphate; bismuth oxychloride.

Red.—Cinnabar; rouge.

Blue.—Prussian blue; ultramarine.

Yellow.—Cadmium sulphide; lead chromate; orpiment.

Green.—Chromic oxide (or by the addition of indigo from *Polygonum tinctorum* (Ait.) to the yellow lacquer).

Black.—Lampblack; iron powder or compounds of iron.

Brown.—Mixture of red and black.

The so-called 'pear-ground' lacquer, used with gold-dust, is prepared with gamboge.

Use of the lacquer.—The prepared surface of the article to be lacquered first receives several coats of the poorer quality mixed with a special clay called *ching-chu*, or in some cases with an inferior clay or with pottery dust. After each coat, the article is kept for several days in a moist atmosphere until the lacquer has set, and it is then rubbed down with pumice to a dull, smooth surface before another coat is given. The final coat is of the better quality lacquer, and the article may be further decorated with a pattern in coloured lacquer. Any joint in the wood is scraped down below the general level of the surface and then filled up with alternate layers of silk and lacquer.

Lacquering is applied to small articles, *e.g.* card-cases, vases, images, &c., either for ornamental purposes or for practical use. Hollow articles of lacquer are made by building up a layer of lacquer and silk on a clay model which is afterwards washed out with water through a hole left for that purpose. (For full details of the manufacture of lacquered ware, *see* Nightingale, J. Indust. and Engineering Chem. 1911, 3, 59; also Workshop Receipts, 3rd series, 306.)

The drying of lacquer at ordinary temperatures is caused by an enzyme (an oxydase) called *laccase*, contained in the sap (Tschirch and Stevens, Arch. Pharm. 1905, 243, 504; J. Soc. Chem. Ind. 1906, 81). During the drying it absorbs 5·75 p.c. of oxygen.

It may also be dried by heat, this process being specially applicable to lacquered articles of glass, porcelain, and papier-mache (Miyama, J. Soc. Chem. Ind. 1909, 318). At 100° it dries in 4–5 hours, at 150° in 30 minutes, and at 180° in 10 minutes. The drying by heat is attended by absorption of oxygen and some decomposition, giving a dark-coloured coating which is harder and more durable than the cold-dried lacquer. Coloured lacquers cannot usually be dried by heat because of the darkening of the lacquer. For a similar reason it is not the practice to use 'driers' in lacquers.

Composition of lacquer.—The main constituent of most lacquers to which their peculiar properties are due, is an unsaturated polyhydric phenol, *urushiol*, having the formula $C_{20}H_{30}O_2$ (Majima, Ber. 1909, 42, 3664; 1912, 45, 2727).

Miyama gives the following analyses of typical specimens of the juice (J. Coll. Eng. Tokyo, 1908, 4, 89; J. Soc. Chem. Ind. 1908, 456):—

	Japanese	Chinese	Indian
Moisture .	17·81–26·72 p.c.	—	—
Urushiol .	64·14–77·63 „	36·88 p.c.	26·39 p.c
Gum .	2·62–7·57 „	23·5 „	37·78 „
Nitrogenous matter .	1·78–2·47 „	—	—

Sun-dried Japanese lacquer contains 94·5 p.c. urushiol.

Urushiol forms a compound with barium hydroxide, and is estimated by titrating with a solution of that base, using phenolphthalein as indicator.

Urushiol may be obtained from lacquer by repeated extraction with alcohol, and is purified by treatment with petroleum spirit. It is a light brown, viscous fluid, sp.gr. 0·9687 at 21·5°/4°, and is readily soluble in most organic solvents. It forms a dimethyl ether and an easily hydrolysable acetyl derivative. On dry distillation it yields various hydrocarbons and polyhydric phenols, but no simple alicyclic hydrocarbon or ordinary terpene (Majima and Cho, Ber. 1907, 40, 4390; Majima, *ibid.* 1909, 42, 1418, 3664; 1912, 45, 2727; Majima and Nakamura, *ibid.* 1913, 46, 4080; *ibid.* 1915, 48, 1597; Majima and Tahara, *ibid.* 1915, 48, 1606). Tschirch and Stevens (*l.c.*) found in the lac an irritant poison, named by them *verniciferol*. This substance may be identical with the compound $C_{15}H_{27}{\cdot}C_6H_3(OH)_2$ found in lacquer, which, according to Toyama and Kayaba (Chem. Soc. Abst. 1918, 114, ii, 143), is poisonous. Lacquer also contains a hydrated and a methylated urushiol which are toxic, and a dimethylated and a hydro-dimethylated urushiol which are non-toxic.

Lacquer poisoning may be produced in susceptible individuals by passing near a lacquer tree or through a store containing lacquered articles.

LAC RESIN *v.* RESINS.

LACTANIN *v.* SYNTHETIC DRUGS.

LACTARIC ACID $C_{14}H_{29}COOH$ is obtained by extracting the fungus *Agaricus integer* with alcohol (Chuit, Bull. Soc. chim. [iii.] 2, 153); m.p. 69·5°–70°.

LACTASE is the enzyme decomposing lactose (milk sugar) to dextrose and galactose. The distribution in animals is limited, being confined entirely to the intestine and generally of young animals only. Lactase has not been found in the mammary gland or milk of animals; this fact is regarded as opposed to the theory that it plays any part in the synthesis of lactose in these tissues (Bradley, J. Biol. Chem. 1913, 13, 431). Plimmer (J. physiol. 1906, 35, 20) found lactase in the cat and the pig during the whole of their lives, but only in the young guinea pig. The gastro-intestinal sac of snails contains a lactase (Bierry, Compt. rend. 1909, 148, 949). It is present in a few torula (*S. fragilis*, *S. kayser*, *S. adametz*, &c.) and in kephir. Lactose is also hydrolysed by the emulsin derived from almonds, which accordingly contains a lactase. There is apparently a difference between kephir and almond lactase, since the hydrolytic activity of the former is restricted mainly by galactose, that of the latter mainly by glucose (Armstrong, Proc. Roy. Soc. 1908, B, 80, 321). According to Stephenson (Bio-Chem. J. 1912, 6, 250), the lactase in the intestines of animals is inhibited only by glucose, and is therefore similar to almond lactase. Lactase also hydrolyses β-methylgalactoside and melibiose. The optimum activity is about 37°. Lactase is precipitated by alcohol, and behaves very similarly to emulsin; its rate of action is governed by the same laws. It has not been fully investigated. E. F. A.

LACTIC ACID or α-**HYDROXYPROPIONIC ACID** (Ger. *Milchsäure*), $CH_3CH(OH)COOH$, was first obtained by Scheele in 1780 from sour milk. Its exact constitution was, however, first ascertained by Liebig and Mitscherlich (Annalen, 7, 47) and by Gay-Lussac and Pelouze (*ibid.* 7, 40). It is widely distributed in nature, occurring in the lesser centaury (*Erythræa Centaurium* [Pers.]) (Habermann, Chem. Zeit. 30, 40); in the sap of the vine; and in most fermented liquids of vegetable origin, especially in sour milk; it is not, however, present in fresh milk. It is found in beet molasses, and owes its origin to the boiling of the sucrose solution with lime in the process of defecation (Schöne and Tollens, J. Soc. Chem. Ind. 1901, 54; Weisberg, *ibid.* 375; Beythien, Parcus and Tollens, Annalen, 255, 228). It has also been found in small quantities in saliva; in the brain and under certain conditions in the gastric juice; in the blood and in urine. The acid obtained by Braconnot, and termed *nanceic acid*, as well as the *thebolactic* acid obtained from opium, have been proved to be identical with common lactic acid. On the other hand, the acid obtained by Berzelius from flesh, and further investigated by Liebig, differs from the ordinary lactic acid in certain of its properties, and is therefore distinguished as *paralactic acid*. This will be described later on.

Lactic acid is formed in the fermentation of various sugars, of mannitol, and of dextrin (*v.* FERMENTATION), and also by the action of caustic alkalis on the sugars. It has also been obtained synthetically in a number of ways, the three most important of which are the following:—

(1) Aldehyde unites with hydrogen cyanide, forming the nitrile

$$CH_3{\cdot}CHO+HCN=CH_3{\cdot}CH(OH)CN$$

and this on treatment with acids is converted into lactic acid (Wislicenus, Annalen, 128, 13, 22).

(2) By the action of alkalis on α-chloropropionic acid (Friedel and Machuca, Annalen, 120, 285)

$$CH_3{\cdot}CHCl{\cdot}COOH+2KOH$$
$$=CH_3{\cdot}CH(OH)COOH+KCl+H_2O$$

(3) By the reduction of pyruvic acid with sodium amalgam, hydriodic acid (Wislicenus, Annalen, 126, 227), zinc (Debus, *ibid.* 127, 332), or electrolytically (Tafel and Friedrichs, Ber. 1904, 3187)

$$CH_3{\cdot}CO{\cdot}COOH+H_2=CH_3{\cdot}CH(OH)COOH$$

These syntheses clearly show that the acid is α-hydroxypropionic acid.

In order to distinguish lactic acid from the allied acids it is frequently called *ethylidene-lactic* or *fermentation lactic acid.*

Preparation.—Lactic acid is usually prepared by the fermentation of sugar. McLauchlan (J. Soc. Chem. Ind. 1909, 734) recommends the following method: 400 grams of commercial glucose are dissolved in 1200 c.c. of hot water, and to this is added 170 grams of whitening or well-powdered calcium carbonate and 20 grams of malt, previously boiled for a few minutes with 100 c.c. of water. The solution is kept simmering for 30 minutes, then cooled to 60°–70°, and after stirring is poured into a narrow-necked bottle, of 2½ litres capacity. The calcium carbonate is rinsed out with water and the solution made up to 1800 c.c. The bottle is placed in an air-bath at 45°, a small quantity of sour milk or caseïn added to start fermentation, and a wad of cotton used to stopper the bottle. The bottle is shaken every few hours for 6 days and when the unfermented sugar is less than 0·4 p.c. the solution is filtered. The final filtrate after concentration should be one litre of 25 p.c. acid. Kassner (Chem. Zentr. 1897, ii. 20) dissolves 300 grams of cane sugar and 15 grams of tartaric acid in 1700 grams of boiling water and allows the solution to stand for several days, the temperature being maintained at 60°; 100 grams of old cheese and a little more than the calculated quantity of finely powdered chalk are then added and fermentation is allowed to proceed with daily stirring for about 3 weeks. Brensch (Annalen, 61, 177) proceeds in a similar manner, but during fermentation keeps the temperature at 30°–35°. Lautemann (*ibid.* 113, 142) replaces the chalk in the original mixture by 2 kilos. zinc white. After about 10 days a magma of zinc lactate together with some mannitol is formed, which may be recrystallised from water. The purified salt obtained by any of these methods is dissolved in boiling water, and precipitated with H_2S, the filtrate evaporated to a syrup, cooled, and separated from mannitol and any undecomposed salt by extraction with ether. The syrup which remains after evaporation of the ether is then warmed on the water-bath.

A large number of micro-organisms are capable of causing lactic fermentation of sugar; these are classified according to their morphological properties, their growth on media, and chiefly their fermentative power (*cf.* Lore and Brooke, U.S. Dept. Agric. Bull, 154, 1). *Bac. acidi lacti*, types i. and ii., and *Bac. lactis ærogenes* are those most commonly occurring, and of these the first named is by far the most plentiful. The solution must be kept neutral, and access of air must be allowed, as well as the necessary nitrogenous food. Its form in a highly nitrogenous saccharine solution, is a double truncated cone, and it has the tendency of all lactic bacteria to link itself together in pairs or short chains (Claflin, J. Soc. Chem. Ind. 1897, 516). Where potato or other starch saccharified by malt is used for the mash, *Bac. Delbreicki*, which ferments maltose, is used as the fermentating organism. (For further particulars of the micro-organisms, *v.* Andreasch, J. Soc. Chem. Ind. 1897, 53; Leichmann and Bazarewski, *ibid.* 1900, 698; Harden, Chem. Soc. Trans. 1901, 624; J. Soc. Chem. Ind. 1901, 921; Hashimoto, *ibid.* 1902, 506; Beijerinck, *ibid.* 1903, 106; Henneberg, *ibid.* 1904, 332; Buchner and Meisenheimer, Annalen, 349, 125; Wehmer, Chem. Zeit. 30, 1033; Heinemann, J. Biol. Chem. 1907, 2, 603.) Lactolase is an enzyme which causes the formation of lactic acid in plant cells (Stoklasa, Chem. Zentr. 1905, i. 265; 1907, i. 828). Malic, succinic, tartaric, and citric acids are all readily converted into lactic acid by certain moulds such as *Pencillium* *glaucum*, *Aspergillus niger*, and *Botrytis cinera* (Bied. Zentr. 1908, 37, 215).

For the preparation of the acid from sugar by the action of caustic alkalis, Kiliani (Ber. 1882, 699) recommends the following method: 500 grams cane sugar are mixed with 250 c.c. water, and 10 c.c. of the sulphuric acid employed later on, and warmed in a flask of 2 litres capacity to 50° for 2 hours. To the well-cooled solution 400 c.c. of caustic soda solution (1 part of caustic to [illegible] part water) are gradually added, the mixture being constantly cooled. The exact quantity of sulphuric acid necessary is then allowed to flow in; the acid is prepared by adding 3 parts H_2SO_4 to 4 parts water, and previously directly compared with the caustic soda solution by titration. A crystal of Glauber's salt is added to facilitate crystallisation, the whole being cooled and well shaken, and allowed to stand 24 hours. The mass is then extracted with 93 p.c. alcohol, filtered off the pump, and half the filtrate neutralised with $ZnCO_3$ on the water-bath, then mixed with the other portion, and the whole allowed to stand 36 hours. The separated zinc salt is filtered off, well pressed, recrystallised from water, and converted into the acid as before.

Just as lactic acid may be obtained by boiling hexoses and hexobioses with caustic alkalis, so it may be obtained from pentoses such as arabinose and xylose (Katsuyama, Ber. 1902, 669; Araki, Zeitsch. physiol Chem. 19, 463) and from cane sugar and raffinose (Beythien, Parcus, and Tollens, Annalen, 255, 222). *Meisenheimer (Ber. 1908, [illegible]009) states that lactic acid is formed in small quantities when glucose*, fructose, or galactose are allowed to stand in dilute sodium hydroxide for many months in the dark.

Manufacture.—There are three stages in the manufacture of lactic acid, the preparation of the saccharine solution, the fermentation process, and the conversion of the fermented liquid into commercial lactic acid. The saccharine solution, which should have a sp.gr. of about 1·075, *i.e.* a saccharine content of 7½–11 p.c., and which should be faintly alkaline or neutral but not acid, is sterilised either by boiling for an hour, or by blowing live steam into the solution for one hour at 95°. It is advantageous to have about 10–15 p.c. of the saccharine matter in the form of cane sugar and the remainder as glucose. After sterilisation, the liquid is conveyed to the fermentation tank, cooled to between 45° and 55°, and impregnated. Where continuous manufacture of lactic acid is carried on, impregnation takes place from a previously fermented liquor where a lively fermentation is in progress; for an original fermentation, milk, which has been kept until it is slightly sour, is used. For efficient working, the lactic acid ferment must be well nourished with nitrogenous matter, the most convenient sources being vegetable matter, *e.g.* as extracted from bran by the action of boiling water and dilute acid. If mineral food is employed, ammonium salts should be in excess of nitrates. Pollak claims that the amount of lactic acid is increased by the repeated addition of ammonium salts in preparing the mashes for fermentation (Eng. Pat. 13193, 1913). As the fermentation proceeds, the temperature is allowed to decrease and the solution is neutralised with milk of lime or chalk in suspension, as the lactic acid bacteria are only healthy in solutions containing between 0·02 and 0·5 p.c. of acid; the fermentation is best completed in from 3 to 6 days. The fermented liquid, which contains calcium lactate with a layer of dead bacteria floating on it, is evaporated and filtered. For a commercial acid, decomposition of the syrupy solution of calcium lactate with sulphuric acid gives an acid of sufficient purity, which may be concentrated *in vacuó*. Iron may be removed by stirring the cooled liquor from the vacuum pans and leaving it to stand for some days, or the addition of a little potassium ferrocyanide has been used. It is important that the lactic acid used by the dyer should be iron-free. The concentrated acid for commercial purposes is about 80 p.c. If a pure acid is required, the solution of calcium lactate is set to crystallise; the solid crystals are pressed to remove mother liquor and may be recrystallised if required (Claflin, J. Soc. Chem. Ind. 1897, 516; Dreher, *ibid.* 1898, 1070; McLauchan, *ibid.* 1907, 734; *cf.* Just, U.S Pat. 868444; J. Soc. Chem. Ind. 1907, 1211; D. R. P. 203306; Chem Zentr. 1908, ii. 1843). Various methods have been patented for the manufacture of lactic acid, differing mainly as to the source of the saccharine solution. Mislin and Lewin (Eng. Pat 10436; Fr. Pat. 355520; J. Soc. Chem. Ind. 1905, 1248) place alternate layers of malt and rye in a suitable apparatus until saccharification of the starch is complete. The must is removed *by pressure and fermented as in above method* (*cf.* Brookes, Eng Pat. 5780; J. Soc. Chem. Ind. 1885, 116; Avery, Pharm. J. Aug. 5, 1882). Jean and Bougard obtain lactic acid from powdered grain or oil-free cake (Fr. Pats. 315325, 315326, 321374; J. Soc. Chem. Ind. 1903, 225), and Claflin uses as the starting material a wort containing about 10 p.c. of fermentable material (U.S. Pat 561163; J. Soc. Chem. Ind. 1907, 985). Boullanger acts on starch or sugar containing substances with a mould such as *Rumex acetosella*, and then proceeds as above (D. R. P. 118083; Chem. Zentr. 1901, i. 650).

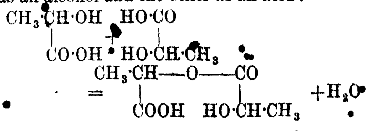
Boehringer states that calcium lactate and sulphuric acid form a paste which is very difficult to work up. The method recommended is to take 200 litres of calcium lactate solution (10°Bé.), obtained from fermentation process, and evaporated to 50 litres; 50 kilos. of a 50 p.c. solution of lactic acid is added and then the calcium lactate is decomposed by sulphuric acid. The solution of lactic acid thus obtained is 50 p.c. (Eng. Pat. 7094; Fr. Pat. 401395; D. R. P. 221112; J. Soc. Chem. Ind. 1909, 674).

Patents have been granted for processes to recover lactic acid from brewers' and distillers' slop and from the waste water of jam factories. One such method consists in neutralising the liquid with milk of lime, partly evaporating and causing the albuminoid substances to coagulate, filtering and allowing the calcium lactate to separate out from the filtrate (Beckers, D. R. P. 104281; Chem. Zentr. 1899, ii. 926; *v.* also Beckers, D. R. P. 113383; Chem. Zentr. 1900, ii. 702; Roehr, U.S. Pat. 823366; J. Soc. Chem. Ind. 1906, 901).

Several processes have been patented for the purification of the acid thus obtained. Waite (Eng. Pat. 13403; D. R. P. 140319; J. Soc. Chem. Ind. 1901, 931), washes the crude acid with amyl alcohol and distils off the solvent from the alcoholic solution of the acid, or washes this solution with water and concentrates the aqueous solution. Blumenthal and Chain (D. R. P. 169992; J. Soc. Chem. Ind. 1907, 279) mix the crude acid with aniline (150 parts 60 p.c. acid with 93 of aniline) and cool to −5°; the precipitate is recrystallised from a small quantity of water, decomposed with steam, and the acid concentrated *in vacuô*. Noerdlinger (Eng. Pat. 26415; Fr. Pat. 364468; D. R. P. 221786; U.S. Pat. 924494; J. Soc. Chem. Ind. 1908, [illegible]45) distils the crude acid in a current of inert gas. The water is first expelled and then pure lactic acid passes over. Laudau (Eng. Pat. 7998, 1915) boils the commercial acid with charcoal while a current of inert gas is passed through. It is concentrated *in vacuô* to 90–95 p.c., and the dextrins present precipitated by alcohol. After standing 24 hours, the liquid is filtered and the alcohol distilled off. Blaise recommends boiling the technical acid for 12 hours with an equal weight of water, and concentrating quickly *in vacuô* at a temperature not above 60° (Bull. Soc. chim. [4] 15, 666). In another process the mixture of calcium sulphate and lactic acid is dried at 130° when lactide and lactic anhydride are formed. After removal of the soluble impurities, pure lactic acid is obtained by hydrolysis in steam (U.S. Pat. 1240708, 1917). Erdmann (D. R. P. 217846; Chem. *Zentr. 1910, i. 701) obtains pure lactic acid from* copper *lactate and water, heated at 150°–250°.*

Properties.—The acid thus obtained forms a syrup of sp.gr. 1·21–1·24, and is soluble in all proportions in water and alcohol, less readily in ether. It is hygroscopic, colourless, and inodorous, but has a very sharp acid taste. The syrup is, however, not the pure acid, but a mixture of the latter with small quantities of water and the anhydride. The pure acid cannot be obtained by evaporation of the aqueous solution, as formation of the anhydride commences before all the water is driven off. Krafft and Dyes (Ber. 1895, 2589; Chem. Zentr. 1896, i. 742) have obtained lactic acid in the form of very hygroscopic white crystals, m.p. 18°, by the distillation of the commercial acid under reduced pressure. Lactic acid is slightly volatile at the ordinary temperatures, lactide is less volatile, and lactic anhydride practically non-volatile (Müller, Bull. Soc. chim. 1896, 15, 1206); lactic acid is volatile in steam, but not sufficiently volatile to be quantitatively separated from aqueous solutions by this means (Utz, Chem. Zeit. 1905, 29, 363). Lactic acid contains an asymmetric carbon atom, and hence can exist in two optically active modifications (*v. infra*). he fermentation lactic acid is optically inactive, ut the acid obtained from the works is someimes optically active. According to McKenzie Chem. Soc. Trans. 1905, 1377), this is due to he fact that the action of the pure culture on ugar is to produce equal amounts of *d*- and *l*-somerides. On converting these into the alcium salts and recrystallising, the crop of rystals which separate is mostly calcium - salt, the active salt remaining in solution. If rystallisation takes place from a concentrated solution and the precipitate is not washed free from mother liquor, the acid obtained will be optically active. This would also be the case if the bacterial action had been such as to produce an excess of one isomeride (*cf.* Pottevin, J. Soc. Chem. Ind. 1899, 700). Wehmer recommends the use of *Oidium lactis* and two mycoderma to decompose lactic acid in liquids where its presence is not desirable (Chem. Zentr. 1903, i. 891). An aqueous solution of lactic acid is stated to decompose in sunlight into acetaldehyde, pyruvic acid, carbon dioxide, and water (Ganassini, Boll. Chim. Farm. 48, 785; Giorn, Farm. Chim. 61, 540), but this is denied by Neuberg (Biochem. Zeitsch. 39, 158). Oxidation of lactic acid with hydrogen peroxide yields pyruvic acid (Fenton and Jones, Chem. Soc. Trans. 1900, 71); with bromine water, pyruvic acid (Ciusa and Piergallini, Atti R. Accad. Lincei, 1914, 821); oxidation by bacteria yields pyruvic acid and ketonic substances (Mazé, Compt. rend. 1918, 81, 1150); with potassium permanganate, pyruvic acid (Aristoff, J. Russ. Phys. Chem. Soc. 1884, 2, 249), acetaldehyde and malic acid (Schoorl, Zeitsch. angew. Chem. 1900, 15, 367); with dilute sulphuric acid at 130°, or by heating alone at 440°–460°, acetaldehyde and formic acid (Nef, Annalen, 335, 296); with chromic acid, acetic acid, and carbon dioxide (Dossios, Zeitsch. Chem. 1866, 451; Chapman and Smith, *ibid.* 1867, 477). Photochemical oxidation in the presence of uranyl or ferric salts yields acetaldehyde and carbon dioxide (Bolin, Zeitsch. physikal. Chem. 87, 490). Oxidation of the *ammonium salt with hydrogen peroxide yields* acetaldehyde, acetic acid, and carbon dioxide (Dakin, J. Biol. Chem. 4, 91). Reduction with hydriodic acid yields propionic acid. Electrolysis of the sodium salt results in the production of acetaldehyde and carbon dioxide (Walker, Chem. Soc Trans. 1896, 1278; Ber. 1894, 467; Kolbe, Annalen, 113, 244). Phosphorus pentachloride converts lactic acid into α-chlorpropionic acid (Walden, Ber. 1895, 1203; Le Bel, *ibid.* 1895, 1923); bleaching powder converts it into chloroform and formic acid (Eberhard, Chem. Soc. Abstr. 1901, i. 357). Lactic acid reduces the nitrates of the heavy metals, *e.g.* bismuth, silver, mercury, cadmium, &c.; cobalt and nickel yield strongly magnetic powders (Vanino and Hauser, Zeitsch. anal. Chem. 1900, 29, 506). When the silver salt is treated with alkyl iodides, the hydrogen of the hydroxyl and carboxyl groups are both attacked (Purdie and Lander, Chem. Soc. Trans. 1898, 296, 300). For thermo-chemical data, *v.* Berthelot and Delépine, Compt. rend. 1899, 129, 920; dielectric constant, electrical conductivity, Drude, Zeitsch. physikal. Chem. 23, 349; Walden, *ibid.* 46, 103; 54, 129.

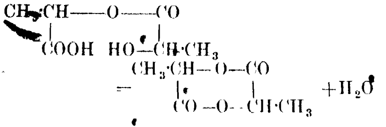
Lactic anhydride, which has been mentioned above, is formed by the elimination of a molecule of water from two molecules of the acid in the following manner, the one molecule acting as an alcohol and the other as an acid:—



$$\begin{array}{lcl} CH_3\cdot CH\cdot OH & & HO\cdot CO \\ \quad | & + & \quad | \\ \quad CO\cdot OH & & HO\cdot CH\cdot CH_3 \end{array} = \begin{array}{l} CH_3\cdot CH—O—CO \\ \quad | \qquad\qquad\quad | \\ \quad COOH \quad HO\cdot CH\cdot CH_3 \end{array} + H_2O$$

This compound, *lactic anhydride* or *lacto-lactic acid*, is at the same time an alcohol, an acid, and an ethereal salt. It is a light yellow amorphous mass, easily soluble in alcohol and ether, insoluble in water, and is decomposed by alkalis, forming salts of lactic acid.

On further heating, another molecule of water is driven off, forming a second anhydride called *lactide*



$$\begin{array}{l} CH_3\cdot CH—O—CO \\ \quad | \qquad\qquad\ | \\ COOH\ \ HO—CH\cdot CH_3 \end{array} = \begin{array}{l} CH_3\cdot CH—O—CO \\ \quad | \qquad\qquad\ | \\ CO—O—CH\cdot CH_3 \end{array} + H_2O$$

This substance, which is a double ethereal salt, is very slightly soluble in water, and forms white needles melting at 124·5° (Bischoff and Walden, Annalen, 279, 71; Nef, *ibid.* 335, 296; Raper, J. Physiol. 32, 216).

Detection and estimation.—On heating lactic acid with potassium chromate and sulphuric acid it is decomposed into formic acid and acetaldehyde. The mixture is distilled and vapours collected in Nessler's solution, giving a yellow precipitate or opalescence (Lassar-Cohn, Annalen, 284, 226; Windisch, J. Soc. Chem. Ind. 1887, 262) Thoms (Apoth. Zeit. 1907, 22, 206) recommends treating a few c.c. of the liquid with 3 or 4 drops of 30 p.c. solution of chromic acid sufficient to impart a bright yellow tint. In the presence of free lactic acid a reddish-brown coloration is produced on warming the solution on the water-bath for 10 minutes. Denigès (Ann. Chim. 18, [viii.] 191) treats the solution with bromine water, and then after the addition of acetic acid a red-violet colour is produced on adding sodium nitroprusside. Lactic acid gives a red coloration with alcoholic guaicol solution and may thus be distinguished from acetic, malic, benzoic and salicylic acids (Hartwig and Saar, Chem Ztg. 1921, 45, 322). Other methods, *v.* Denigès, Bull. Soc chim. 1909, 5, 647; Croner and Cronheim, J. Soc. Chem. Ind. 1905, 1258; Herzog, Annalen, 1907, 351, 263. The following process has been recommended by Jean (Ann Chim. Anal. Appl. 1900, 5, 285) for estimating the commercial acid. (i.) Total acidity is determined as H_2SO_4; (ii.) free acids by evaporating three times to dryness on the water-bath; (iii.) lactic acid by evaporating 10 c.c. to dryness several times, and dissolving the residue in water. The solution is heated to boiling, neutralised with barium carbonate, and then filtered and evaporated to dryness in a platinum dish. The residue is incinerated to carbonate, extracted with boiling water, collected on a filter, well washed, and dissolved in a known volume of decinormal hydrochloric acid. The solution is heated to remove the carbon dioxide, titrated with decinormal alkali, and the volume of N/10-hydrochloric acid neutralised by the carbonate formed by subtraction. This number of c.c. × 0·009 gives weight of lactic acid originally present. To estimate the amount of lactic acid and lactic anhydride present in a sample of lactic acid, the following process is used: (i.) dilute sample with water and titrate with normal sodium hydroxide, using phenolphthalein as an indicator; (ii.) add a known excess of sodium hydroxide and titrate back with acid; (i.) gives actual amount of acid and (ii.) of anhydride (Philip, Collegium, 1906, 88; Kunz, Chem. Zentr. 1901, i. 791; Bellet, Bull. Soc. chim. 1913, 13, 565). Other methods, *v.* Ulzer and Seidel, Monatsh. 18, 138; Paessler, Collegium, 1907, 388, 396; Phelps and Palmer, J. Amer. Chem. Soc. 1917, 136. Estimation in wines, *v.* Kunz, Chem. Soc. Abstr. 1901, ii. 700; 1903, ii. 701; Sostegni and Prandi, Chem. Zentr. 1903, ii. 469; Müller, Bull. Soc. chim. 1896, 15, [iii.] 1203; Parthiel, Chem. Soc. Abstr. 1903, ii. 189; Arch. Pharm. 241, 401; Paris, Chem. Zentr. 1908, i. 773; Trummer, Chem. Zentr. 1908, ii. 101; Heiduschka and Quincke, Arch. Pharm. 245, 458. In milk, *v.* Thörner, Chem. Zeit. 16, 1469. 1519. In urine, *v.* Proc. Physiol. Soc. 1909, v.–vii.; J. Physiol. 39; Biochem. Zeitsch. 68, 175. In gastric juice, *v.* De Jong, Chem. Zentr. 1896, ii. 806. In the presence of pyruvic acid, Czapski, Biochem. Zeitsch. 71, 167. For the extraction of lactic acid from the tissues, amyl alcohol is recommended as the most suitable solvent, Ohlsson, Chem. Soc. Abstr. 1916, ii. 542.

Technical uses.—Lactic acid is used by the woollen dyer as an assistant in mordanting with potassium dichromate and its advantages over tartaric and oxalic acids are its greater reducing power, the greater solubility of itself and its salts, and the fact that it is less corrosive It gives the wool a very fine, soft 'handle and a beautiful lustre. *Lactolin*, which consists of equal parts of lactic acid and potassium lactate, is stated to be superior to lactic acid, which is in itself superior to tartar (Claflin, *l.c.*; Norton and Tuttle, J. Soc. Chem. Ind. 1891, 263; Hoffmann, *ibid.* 1896, 196, 540; Dreher, *ibid.* 1896, 448; 1898, 1070; 1899, 491; Kielmeyer, *ibid.* 1899, 368; Kapff, *ibid.* 1900, 659; Fuchs, Chem Zentr 1897, i. 1183; Archer, J. Soc. Chem. Ind. 1897, 140; Düring, Bull. Soc. Ind. Mulhouse, 1902, [v.] 3; Paessler and Appelius, Collegium, 1903, 152, 153, 164, 169). Aniline lactate is used in producing aniline black on cotton (Goldovsky, Bull. Soc. Ind. Mulhouse, Jan. 9, 1900; Schener and Schoellkopf, *ibid.* 1901, 102; Düring, Chem. Zentr. 1905, i. 1515; D. R. P. 96600; J. Soc Chem. Ind. 1899, 1119). The double lactate of calcium and antimony is used in mordanting cotton, and as a substitute for glycerin and tartaric acid in printing fabrics (Dreher, J. Soc. Chem. Ind. 1898, 919, 921). For methods of obtaining double lactates of antimony and calcium or of antimony and alkalis or alkaline earths, *v.* Moritz, Zeitsch. angew. Chem. 17, 1143; Akt. Ges. "Reavler Chem. Fab. R. Mayer, D. R. P. 136135; Chem. Zentr. 1902, ii. 1286; Ch. Fab. von Heyden, D. R. P. 184202; Chem. Soc. Abstr. 1907, i. 888; Boehringer, D. R. P. 98939; Chem. Zentr. 1898, ii. 1231; Ch. Werke Schuster and Wilhelmj, D. R. PP. 216158, 217606; Chem. Zentr. 1909, ii. 1908; 1910, i. 70[illegible].

A solution containing the lactates of aluminium, calcium, and tin has been used instead of the above (Oswald, Bull. Soc. Ind. Mulhouse, 1909, 343), whilst Boehringer (D. R. P. 91230; Chem. Zentr. 1897, i. 1189) employs zinc lactate for the same purpose. Lactolin and sulphuric acid are used in hat dyeing (Düring, J. Soc. Chem. Ind. 1900, 660; 1901, 470) and lactic acid, free from traces of iron, is used as a discharge for

Turkey red (Düring, *ibid.* 1900, 1013). It has also been used as a solvent for dyestuffs insoluble in water (Dreher, *ibid.* 1897, 1014; 1898, 919, 921).

Lactic acid is used in tanning for colouring, bating, and plumping. In preparing the skins it completely removes the lime, ensures a fine even grain, and does not dissolve the hide substance. It is easier to control than the bran drench, which is also used for this purpose, and which owes its efficiency to the lactic acid produced during the fermentation of the bran (Claflin, J. Soc. Chem. Ind. 1901, 210, 596, 730, 913; Paessler and Appelius, *ibid.* 1902, 1461, 57; 1903, 1201). It is also used in the preparation of yeast (Büchler, *ibid.* 1901, 376) and in the distillery, *e.g.* to check the bacterial development in the 'Hefengut' mash (Moritz, *ibid.* 1899, 778).

Lactic acid is also used for medicinal purposes in cases of laryngeal tuberculosis and of infantile diarrhœa. It dissolves false membrane and a solution of 1 part of acid in 6 parts of water is employed in the local treatment of diphtheria and croup. Local applications are used in stopping the growth of venereal worts and in treatment of tuberculous ulcers, lupus, and epithelioma. Calcium lactate is used in the treatment of rheumatism. For pharmaceutical purposes, the acid must be colourless and inodorous, and have a sp.gr. of at least 1·21, and should leave scarcely any residue on ignition. It should be unaffected by NH_3 and $(NH_4)_2S$, should give, at most, only a faint opalescence with $BaCl_2$, $AgNO_3$, $(NH_4)_2C_2O_4$, and should give no precipitate on boiling with Barreswil's (Fehling's) solution. For its influence in human dietary, *v.* J. Soc. Chem. Ind. 1920, 236.

Esters. The esters of lactic acid may be prepared by treating a salt of lactic acid with sulphuric acid or gaseous hydrogen chloride and the corresponding alcohol; or the anhydride (lactide) may be treated with alcohol in the presence of aluminium sulphate or titanic acid anhydride as catalyst, D. R. P 278,487. The product is distilled *in vacuô*, whereby the pure ester is obtained. By treating the pure ester with steam, distilling off the alcohol and concentrating, the pure acid is obtained (Ch. Fab. Güstrow, Hillringhaus and Heilmann, D. R. P. 171835; Chem. Zentr. 1906, ii. 470).

Methyl ester. Colourless liquid, b.p. 144·8°; sp.gr. 1·0898 at 19° (Schreiner, Annalen, 197, 12).

Ethyl ester. Colourless liquid, b.p. 154–5°; sp.gr. 1·0308 at 19° (Schreiner, *l.c.*; Friedel and Wurz, Ann. Chim. [iii.] 63, 102; Bruggen, Annalen, 148, 227).

Ethylidene ester. Prepared by heating acetaldehyde and lactic acid at 120°–170° for some hours: colourless liquid, b.p. 150°–151·5° (Leipen. Monatsh. 9, 45).

Glyceryl mono- and di-lactates (*v.* Kalle & Co. D. R. P. 216917; Chem. Zentr. 1910, i. 214).

Salts. The salts of lactic acid are all soluble in water, many so readily that they are very difficult to obtain crystalline. They are obtained by direct neutralisation of the free acid, or by double decomposition from the calcium salt.

The K, Na salts are very hygroscopic, and only the latter has been obtained crystalline (Wislicenus, Annalen, 125, 49; Engelhardt and Maddrell, *ibid.* 63, 88; Brüning, *ibid.* 104, 192).

Ammonium lactate is crystalline and very hygroscopic. On distilling it *in vacuô*, acid ammonium lactate, a syrup (b.p. 140° at 10 mm.) passes over (D. R. P 247,240; J. pr. Chem. [2] 87, 258).

Calcium lactate $(C_3H_5O_3)_2Ca,5H_2O$ is usually obtained direct from sugar in the preparations of lactic acid (*v. supra*) In small quantities it is sometimes prepared by neutralising lactic acid with chalk. It forms cauliflower-like aggregates of microscopic rhombic needles, which are soluble in 9·5 parts of cold, much more readily in hot water, and also soluble in alcohol. It loses its water of crystallisation at 100°, and at 250°–275° loses another molecule of water, forming *calcium dilactate* $(CH_3{\cdot}CH)_2{\cdot}O(CO_2)_2Ca$. The product is a vesicular mass, from which alcohol extracts some unaltered calcium lactate, and leaves the new compound behind as a very slightly soluble substance (Friedel and Würtz Ann. Chim. Phys. [iii.] 63, 114).

Barium lactate $(C_3H_5O_3)_2Ba,4H_2O$ crystallises with great difficulty, forming cauliflower-like aggregates. It does not lose all its water of crystallisation at 100° (Meyer, Ber. 1886, 2454).

Magnesium lactate $(C_3H_5O_3)_2Mg,3H_2O$ is prepared by dissolving lactic acid syrup in 10 times its bulk of water, and neutralising with basic magnesium carbonate. The solution is evaporated until a skin forms, and then allowed to crystallise. It forms small light prismatic crystals, which frequently unite to form crusts. It dissolves in 28 parts of cold and 6 parts of hot water, forming a neutral very bitter solution. It loses its water of crystallisation at 100°.

Zinc lactate $(C_3H_5O_3)_2Zn,3H_2O$ is best obtained direct from sugar by neutralising the lactic acid produced with zinc carbonate or zinc white (Lautemann, Annalen, 113, 142, Kiliani, Ber. 1882, 659). It crystallises better than any other lactate, and forms colourless, well-developed, four-sided rhombic prisms. It loses its water of crystallisation *in vacuô* or at 100°. It dissolves in 53 parts of water at 15°, and in 6 parts at 100°, forming an acid, bitter-tasting solution. It is very slightly soluble in alcohol (Strecker, Annalen, 105, 316).

Ferrous lactate $(C_3H_5O_3)_2Fe,3H_2O$. This salt was introduced into pharmacy by Gélis and Conté in 1840, and was again recommended in 1847 by Engelhardt and Maddrell (*l.c.*). It is best prepared from crude calcium lactate in the following manner. The crude salt is recrystallised from water to which a little lime has been added, and if necessary the operation repeated. To the conc. aqueous solution of the purified salt the theoretical quantity of ferrous chloride is added, and the mixture allowed to stand for 3 days in a cool place. When no more crystals form the precipitated salt is filtered off, washed with a little alcohol, and dried at 50°.

Ferrous lactate forms greenish-white crusts of needles, or a similarly coloured crystalline powder. It dissolves at the ordinary temperature in 48 parts, and at 100° in 12 parts of water, forming an acid solution with a sweetish chalybeate taste. The solution becomes yellow, and then brown, in the air, ferric lactate being formed, and also undergoes alteration on evaporation in the air, leaving a hygroscopic residue containing ferrous and ferric lactates and some free acid. The dry salt is unaltered in the air, and loses its water of crystallisation when heated at 100° in a current of hydrogen.

Silver lactate $C_3H_5O_3Ag,\frac{1}{2}H_2O$ is prepared by treating freshly prepared lactic acid, after cooling, with silver oxide, evaporating the solution in the dark *in vacuô* at the ordinary temperature. It forms colourless needles, soluble in 20 parts of cold water, insoluble in cold, but readily soluble in hot alcohol. On heating the salt in the dark for 3 hours at 80°, anhydrous silver lactate is obtained (Klimenko, J. Russ. Chem. Soc. 12, 97; Berthelot and Delépine, Compt. rend. 129, 920).

Bismuth lactate $BiC_6H_9O_6,7H_2O$ is prepared by the slow dissolution of freshly precipitated bismuth hydroxide in lactic acid slightly diluted with water. The solution gradually deposits needles of the hydrated salt; on heating to 105° this yields the anhydrous salt, which is very sparingly soluble in water The latter may be obtained by digesting freshly precipitated bismuth hydroxide in lactic acid at 100°. It forms rhombic tablets which decompose slightly when boiled with water for some time (Telle, Arch. Pharm. 1908, 246, 484).

Mercury lactates. *Mercurous lactate*

$$(C_3H_5O_3)_2Hg,HgO$$

is prepared by dissolving freshly precipitated mercurous oxide in dilute lactic acid, which has previously been heated with water to destroy the anhydride which it contains. The solution is allowed to evaporate in a desiccator over sulphuric acid when the salt separates in short white prismatic needles. It is not completely soluble in water, hydrolysis occurring with the formation of a basic lactate, which then decomposes into mercuric lactate and mercury. *Mercuric lactate* $(C_3H_5O_3)_2Hg$, prepared in a similar manner from lactic acid and mercuric oxide, forms colourless prismatic needles, readily soluble in water. On boiling the aqueous solution, mercurous lactate, acetaldehyde, lactic acid, and carbon dioxide are produced (Guerbet, Bull. Soc. chim. 1902, 27, [iii.] 803).

Glucinium lactate (*v.* Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 39, 936; Glassmann, Ber. 1908, 33).

Cerous lactate (*v.* Morgan and Cahen, Pharm. J. 1907, 78, 428).

Optically active acids. As has already been stated, lactic acid can be resolved into two optically active components. This resolution has been effected by the fractional crystallisation of zinc ammonium lactate (Purdie and Walker, Chem. Soc. Trans. 1893, 1143; 1895, 616); of the strychnine salts (Purdie and Walker, *ibid.* 1892, 754; morphine salts (Irvine, *ibid.* 1906, 935); and of the quinine salts (Jungfleisch, Compt. rend. 1904, 139, 56, 203; 1905, 140, 719; 1906, 142, 515). Asymmetric syntheses have been made by the reduction of the *l*-menthyl (McKenzie, Chem. Soc. Trans. 1905, 1373), *l*-bornyl (McKenzie and Wren, *ibid.* 1906, 688), and *d*-amyl (McKenzie and Müller, *ibid.* 1909, 544) salts of pyruvic acid.

Paralactic acid (Sarcolactic acid, *d*-lactic acid) is present in flesh, in the blood, in muscles, in the thymus and thyroid and other animal organs (Berlinbauer, Chem. Zentr. 1888, 757; Salomon, Chem. Soc. Abstr. 1889, 64; Asker and Jackson, Zeit. Biol. 41, 393; Moscatelli, Zeitsch. physiol. Chem. 12, 416; Griffiths, Chem. News, 91, 147; Werther, Chem. Soc. Abstr. 1890, 348; Inouye and Kondo, Zeitsch. physiol. Chem. 54, 481; Frew, *ibid.* 60, 15; Moriya, *ibid.* 43, 397). In muscle tissue, the amount increases with the degree of muscular activity. According to Embden (Zeitsch. physiol. Chem. 93, 1) a compound of phosphoric and lactic acids occurs as an intermediate metabolic product.

It is obtained from extract of meat by dissolving in 4 parts of warm water, adding 3 times the volume of 90 p.c. alcohol, and evaporating the filtrate to a syrup. This is again precipitated with alcohol, filtered, and evaporated, then acidified with H_2SO_4, and extracted with ether (Wislicenus, Annalen, 167, 302). The crude acid may be purified by conversion into the zinc salt. If *Penicillium glaucum* is allowed to grow in the solution of the inactive ammonium lactate, the *d*- modification alone will remain (Lewkowitsch, Ber. 1883, 2720; Linossier, Bull. Soc. chim. [iii.] 6, 10). *Micrococcus acidi paralacti*, an anaërobic micrococcus formed in the preparation of the *Rauschbrand bacillus*, is found to convert sugar into paralactic acid (Nencki and Sieber, Monatsh. 10, 532).

Paralactic acid is a syrup which can only be distinguished from lactic acid by the fact that it rotates the plane of polarisation to the right, whereas lactic acid is inactive. The salts strongly resemble the lactates, but are somewhat more soluble in water. The methyl ester boils at 143°-145° and has sp.gr. 1·1017 at 15°/16°; and the ethyl ester, b.p. 152°–154°, sp gr. 1·0414 at 15°/16° (Frankland, Chem. Soc. Proc. 1895, 54). Further details as to rotatory power of acid and derivatives, *v.* Walker, Chem. Soc. Trans. 1895, 914; Purdie and Williamson, *ibid.* 1896, 827; Guye and Melikian, Compt. rend. 123, 1291; Henderson, and Prentice Chem. Soc. Trans, 1902, 658; 1903, 259; Wassmer and Guye, J. Phys Chem. 1903, i. 257; Purdie and Irvine, Chem. Soc. Trans. 1899, 484; Walker, J. Phys Chem. 13, 574.

l-**Lactic acid** has not been found in nature. It is prepared by the resolution of the inactive acid (*q.v.*); by the fermentation of sugar with *Bacillus acidi lævolacti* (Schardinger, Monatsh. 11, 545) or with a lævolactic ferment obtained from pears (Tate, Chem. Soc. Trans. 1893, 1263). It is similar in properties to *d*-lactic acid, with the exception that it rotates the plane of polarisation to the left.

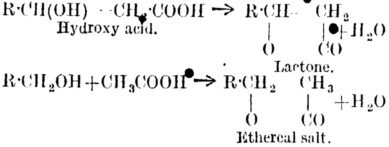
Besides these acids, another isomeric acid remains to be described. *Hydracrylic acid, ethylene-lactic acid* or *β-hydroxypropionic acid* $CH_2(OH)CH_2CO_2H$ is prepared by the action of moist silver oxide on β-iodopropionic acid (Sokolow, Annalen, 150, 167; Wislicenus, Annalen, 166, 10); by heating the sodium salt of acrylic acid with sodium hydroxide at 100° (Linnemann, Ber. 1875, 1095); and by the action of prussic acid on ethylene chlorhydrin and saponification of the resulting nitrile (Wislicenus, Annalen, 128, 1; 167, 346; Erlenmeyer, *ibid.* 191, 268). It forms a syrup which decomposes into water and acrylic acid on heating. Chromic acid oxidises it into oxalic acid and carbon dioxide, and silver oxide converts it into glycollic acid. Wislicenus also obtained from flesh, in addition to paralactic acid, an acid which he believed to be identical with this ethylene-lactic acid, but it has been shown (Siegfried, Ber. 1889, 2713) that this is in reality *acetyllactic acid.*

Atrolactinic acid (*αα-phenylhydroxypropionic acid*) $CH_3{\cdot}C(C_6H_5)OH{\cdot}CO_2H$. Prepared by the action of fuming hydrochloric acid on acetophenone hydrocyanide (Spiegel, Ber. 1881, 14, 1353; Tiemann and Köhler, *ibid.* 1980); colourless needles, m.p. (anhydrous) 93°–94°.

LACTIC FERMENTATION GUM *v.* GUMS.

LACTOLIN. Trade name for potassium dilactate used as a mordant.

LACTONES. Generally speaking a lactone is formed by the elimination of water from a hydroxyl group and a carboxyl group present in the same molecule. They may therefore be regarded as internal salts corresponding with the external salts which are known as the ethereal salts or esters:



$$R{\cdot}CH(OH){-}CH_2{\cdot}COOH \rightarrow \underset{O\quad CO}{R{\cdot}CH{-}CH_2} + H_2O$$

Hydroxy acid. Lactone.

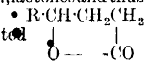
$$R{\cdot}CH_2OH + CH_3COOH \rightarrow \underset{O\quad CO}{R{\cdot}CH_2\quad CH_3} + H_2O$$

Ethereal salt.

The lactones are therefore derived from that class of organic compounds known as the hydroxy acids. The hydroxy acids are divided into several series depending on the position of the hydroxyl group in respect to the carboxyl group and are named α-, β-, γ-, &c., hydroxy acids according as the hydroxyl group is in the α-, β,- γ-, &c., position in respect to the acid group, thus:

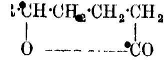
$R{\cdot}CH(OH){\cdot}COOH$
(α) — α-Hydroxy acid
$R{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH$
(β) (α) — β-Hydroxy acid
$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
(γ) (β) (α) — γ-Hydroxy acid
$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
(δ) (γ) (β) (α) — δ-Hydroxy acid
$R{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$
(ε) (δ) (γ) (β) (α) — ε-Hydroxy acid
$·CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2COOH$
(ζ) (ε) (δ) (γ) (β) (α) — ζ Hydroxy acid

The lactones derived from these acids are amed accordingly α-, β-, γ-, &c., lactones and thus γ-lactone would be constituted



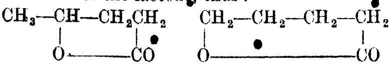
$$\underset{O\;-\;-CO}{R{\cdot}CH{\cdot}CH_2CH_2}$$

nd a δ-lactone would have the structure



$$\underset{O\;\text{———}\;CO}{R{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2}$$

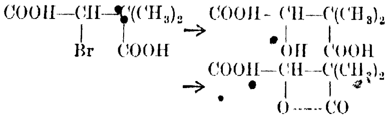
Nomenclature.—The name of the lactone is sually taken from the trivial name of the acid rom which the corresponding hydroxy acid is erived, as for example, butyrolactone from -hydroxybutyric acid, valerolactone from -hydroxyvaleric acid. In those cases where the formation of two isomeric lactones is possible the prefix γ- or δ- is added to indicate the order of the lactone, thus:



$$\underset{O\text{———}CO}{CH_3{-}CH{-}CH_2CH_2} \qquad \underset{O\text{—————}CO}{CH_2{-}CH_2{-}CH_2{-}CH_2}$$

γ-Valerolactone. δ-Valerolactone.

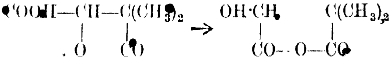
α-Lactones are not known, and in only a few exceptional cases has the formation of β-lactones been observed. Thus Baeyer and Villiger (Ber. 1897, 30, 1954; compare also Fichter and Hirsch, *ibid.* 1900, 33, 3273) have shown that when α-bromo-αα′-dimethylsuccinic acid is treated with moist silver oxide the β-lactone of dimethylmalic acid is formed:



$$\underset{Br\qquad COOH}{COOH{-}CH{-}C(CH_3)_2} \rightarrow \underset{OH\quad COOH}{COOH{-}CH{-}C(CH_3)_2} \rightarrow \underset{O\text{----}CO}{COOH{-}CH{-}C(CH_3)_2}$$

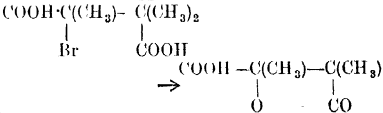
β-Lactone.

This compound crystallises in rhombic plates containing 1 mol. of water, and melts at 51°–55°; it loses this water of crystallisation at 45° in a vacuum. When distilled under diminished pressure it passes by rearrangement into the anhydride of αα-dimethylmalic acid



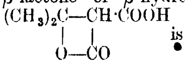
$$\underset{O\qquad CO}{COOH{-}CH{-}C(CH_3)_2} \rightarrow \underset{CO{-}O{-}CO}{OH{\cdot}CH\qquad C(CH_3)_2}$$

In the same way, trimethylbromosuccinic acid is converted into the β-lactone of trimethylmalic acid (Komppa, Ber. 1902, 35, 534)



$$\underset{Br\qquad COOH}{COOH{\cdot}C(CH_3){-}C(CH_3)_2} \rightarrow \underset{O\qquad CO}{COOH{-}C(CH_3){-}C(CH_3)_2}$$

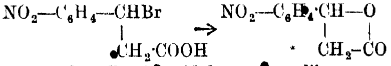
The formation of a similar compound has been recorded by Meldrum (Chem. Soc. Trans. 1908, 93, 598), who finds that when acetone is condensed with malonic acid in the presence of acetic anhydride containing a little sulphuric acid, the β-lactone of β-hydroxy*iso*propylmalonic acid



$$\underset{O{-}CO}{(CH_3)_2C{-}CH{\cdot}COOH}$$

is formed. This substance crystallises from acetone in transparent four-sided plates melting at 97°.

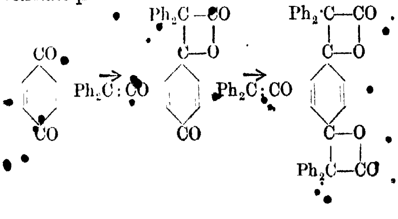
β-Lactone formation occurs in the aromatic series from β-hydroxy acids having a phenyl-group, in which strongly negative groups are present, attached to the β-carbon atom. Thus the lactones of *o*-, *m*-, and *p*-nitrophenyl-β-lactic acids are formed when the corresponding nitrophenyl-β-bromopropionic acids are treated with cold aqueous sodium carbonate



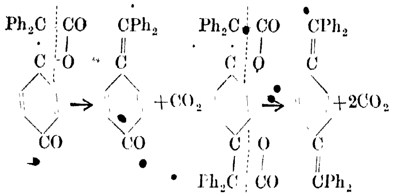
$$\underset{CH_2{\cdot}COOH}{NO_2{-}C_6H_4{-}CHBr} \rightarrow \underset{CH_2{-}CO}{NO_2{-}C_6H_4{\cdot}CH{-}O}$$

o-Nitrophenyllactic acid lactone readily passes into indigo when boiled with glacial acetic acid.

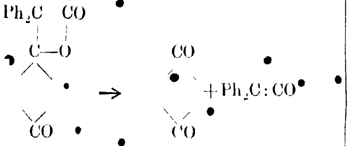
A remarkable series of aromatic β-lactones have been prepared by Staudinger by condensing diphenylketene with various quinones. When, for example, quinone itself is used the reaction proceeds in two stages, a di-β-lactone being the ultimate product—



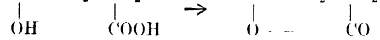
Both lactones eliminate carbon dioxide when heated—



but in the former case a certain amount of fission takes place in the other direction (Ber 1908, 41, 1355):—

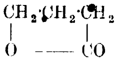


γ-Lactones. The remarkable tendency which exists for the formation of the five-membered ring causes the γ-hydroxy acids to be, usually, unstable at the ordinary temperature and to pass, with elimination of water, into the γ-lactone

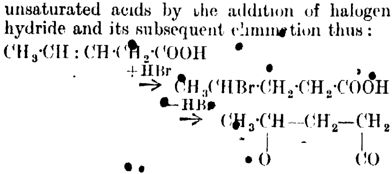


$$\begin{array}{ccc}\mathrm{R{\cdot}CH}&\mathrm{—CH_2—}&\mathrm{CH_2}\\ |&&|\\ \mathrm{OH}&&\mathrm{COOH}\end{array}\rightarrow\begin{array}{ccc}\mathrm{R—CH}&\mathrm{—CH_2—}&\mathrm{CH_2}\\ |&&|\\ \mathrm{O}&\text{——}&\mathrm{CO}\end{array}$$

γ-Hydroxy acid γ-Lactone

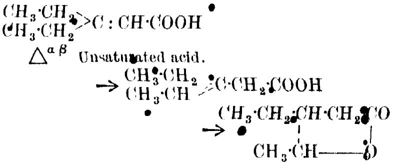
The tendency for the formation of the inner anhydride is so great that the change from the hydroxy acid to the lactone is usually effected by merely raising the temperature of an aqueous solution of the acid and in many cases the lactone exists in aqueous solution at the ordinary temperature. The simplest member of the class, butyrolactone  $\begin{array}{ccc}\mathrm{CH_2{\cdot}}&\mathrm{CH_2{\cdot}}&\mathrm{CH_2}\\ |&&|\\ \mathrm{O}&\text{——}&\mathrm{CO}\end{array}$, was discovered by Saithew in 1873, although certain naturally occurring lactones, such as coumarin and meconine (*q.v.*), were known before that time. (For a general description of the lactones, compare E. Hzelt, Ahrens' Samm. 1903, 8, 83.)

Formation.—The methods usually adopted for the preparation of γ-hydroxy acids, that is of the γ-lactones, may be briefly summarised as follows: (1) The transformation of the $\Delta^{\beta\cdot\gamma}$ unsaturated acids by the addition of halogen hydride and its subsequent elimination thus:



$$\mathrm{CH_3{\cdot}CH:CH{\cdot}CH_2{\cdot}COOH}\xrightarrow{+\mathrm{HBr}}\mathrm{CH_3CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH}\xrightarrow{-\mathrm{HBr}}\begin{array}{ccc}\mathrm{CH_3{\cdot}CH}&\mathrm{—CH_2—}&\mathrm{CH_2}\\ |&&|\\ \mathrm{O}&&\mathrm{CO}\end{array}$$

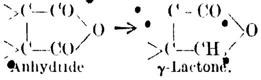
The $\Delta^{\beta\gamma\cdot}$ unsaturated acids are also transformed into the γ-lactones either by merely heating them alone or by warming them with a mixture of equal volumes of concentrated sulphuric acid and water at 140° (Fittig. Ber. 1894, 27, 2667; Annalen, 1894, 283, 51). In the latter instance, the same change is shown by those $\Delta^{a.\beta\cdot}$ unsaturated acids which have two alkyl groups on the β-carbon atom. Thus Fichter, Kiefer, and Bernoulli (Ber. 1909, 42, 4710) find that when ββ-diethylacrylic acid is warmed for a short time with 60 p.c. aqueous sulphuric acid, it is converted into β-ethyl-γ-valerolactone



$$\begin{array}{l}\mathrm{CH_3{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CH_2}\end{array}\!\!>\mathrm{C:CH{\cdot}COOH}\rightarrow\begin{array}{l}\mathrm{CH_3{\cdot}CH_2}\\ \mathrm{CH_3{\cdot}CH}\end{array}\!\!>\mathrm{C{\cdot}CH_2{\cdot}COOH}\rightarrow\begin{array}{ccc}\mathrm{CH_3{\cdot}CH_2{\cdot}CH}&\mathrm{{\cdot}CH_2{\cdot}}&\mathrm{CO}\\ |&&|\\ \mathrm{CH_3{\cdot}CH}&\text{——}&\mathrm{O}\end{array}$$

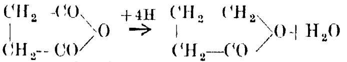
$\Delta^{\alpha\beta}$ Unsaturated acid. γ-Lactone.

(2) The relation between the anhydrides of the dibasic acids and the γ-lactones, which is illustrated by the expression :—



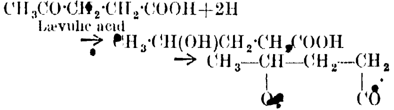
Anhydride γ-Lactone.

indicates that the last-named compounds can be derived from the anhydrides by reduction. Thus butyrolactone is formed when succinic anhydride is reduced by sodium amalgam (Fichter and Herbrand, Ber. 1896, 29, 1192):



Succinic anhydride Butyrolactone.

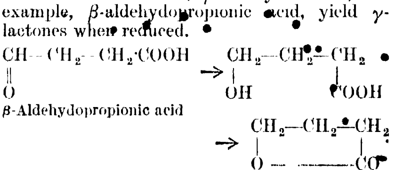
(3) The sodium salts of γ-hydroxy acids are also formed when γ-ketonic acids, such as lævulic acid, are reduced by sodium amalgam, thus:



$$\underset{\text{Lævulic acid}}{\mathrm{CH_3CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH}}+2\mathrm{H}\rightarrow\mathrm{CH_3{\cdot}CH(OH)CH_2{\cdot}CH_2COOH}\rightarrow\begin{array}{ccc}\mathrm{CH_3—CH}&\mathrm{—CH_2—}&\mathrm{CH_2}\\ |&&|\\ \mathrm{O}&&\mathrm{CO}\end{array}$$

γ-Valerolactone.

In a similar manner, β-aldehyde acids, for example, β-aldehydopropionic acid, yield γ-lactones when reduced.



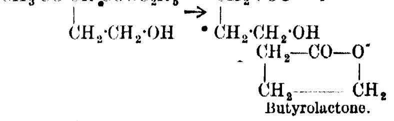
$$\begin{array}{l}\mathrm{CH—CH_2—CH_2{\cdot}COOH}\\ \|\\ \mathrm{O}\end{array}\rightarrow\begin{array}{ccc}\mathrm{CH_2}&\mathrm{—CH_2—}&\mathrm{CH_2}\\ |&&|\\ \mathrm{OH}&&\mathrm{COOH}\end{array}\rightarrow\begin{array}{ccc}\mathrm{CH_2}&\mathrm{—CH_2—}&\mathrm{CH_2}\\ |&&|\\ \mathrm{O}&\text{——}&\mathrm{CO}\end{array}$$

β-Aldehydopropionic acid Butyrolactone.

(4) The alkyl salts of γ-hydroxy acids may be formed by the condensation of chlorhydrins of the type $\mathrm{CH_2Cl{\cdot}CH_2OH}$ with the sodium compounds of ethyl acetoacetate and its homologues, thus:

$$\mathrm{CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5+CH_2Cl{\cdot}CH_2OH}$$
$$\rightarrow\mathrm{CH_3{\cdot}CO{\cdot}CH(COOC_2H_5)CH_2{\cdot}CH_2OH+NaCl}$$

When this ethyl salt is hydrolysed with baryta, the acetyl group is eliminated and the barium salt of the hydroxy acid, which is then formed, is converted into the γ-lactone by the action of dilute mineral acids:

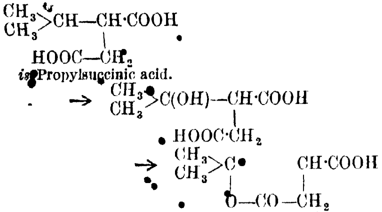


$$\begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5}\\ \qquad\quad |\\ \qquad\mathrm{CH_2{\cdot}CH_2{\cdot}OH}\end{array}\rightarrow\begin{array}{l}\mathrm{CH_2{\cdot}COO^{Ba/_2}}\\ |\\ \mathrm{CH_2{\cdot}CH_2{\cdot}OH}\end{array}\quad\begin{array}{ccc}\mathrm{CH_2}&\mathrm{—CO—}&\mathrm{O}\\ |&&|\\ \mathrm{CH_2}&\text{——}&\mathrm{CH_2}\end{array}$$

Butyrolactone.

(5) The formation of certain γ-lactones may

also be effected by taking advantage of the fact that the tertiary hydrogen atom of the system $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!>\!CH—$ is readily oxidised to hydroxyl by alkaline permanganate. Thus *iso*propyl-succinic acid passes on oxidation into terebic acid (Lawrence, Chem. Soc. Trans. 1899, 75, 527).

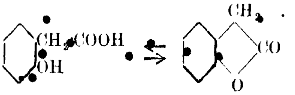


*iso*Propylsuccinic acid.

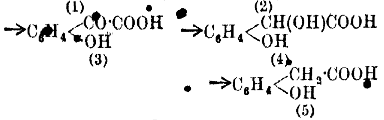
Terebic acid.

(6) The methods of formation of γ-lactones of the aromatic series are similar to those employed with aliphatic compounds, but for the sake of convenience the substances belonging to this class may be divided into three sections. (*a*) The γ-lactones which are derived from hydroxy acids having the hydroxyl group in the ortho- position in the benzene nucleus to a side chain bearing a carboxyl group. (*b*) The γ-lactones which are formed when both the hydroxyl and carboxyl groups are attached to the side chain. (*c*) The γ-lactones formed from compounds having the hydroxyl group in the side chain and the carboxyl group attached to the ortho- position in the benzene nucleus.

o-Hydroxyphenylacetic acid may be given as an illustration of compounds included under section (*a*). This acid, unlike the γ-hydroxy acids of the aliphatic series, can be isolated in the free state, but passes into the γ-lactone on distillation :



The lactone is again converted into the acid on shaking with water. The method employed for the preparation of *o*-hydroxyphenylacetic acid is as follows (Baeyer and Fritsch, Ber. 1884, 17, 973 ; compare also Stoermer, Annalen, 1900, 313, 83 ; Ber. 1901, 34, 1807). Isatin (1) is converted into *o*-aminobenzoylformic acid, (2) by the action of alkali, and this substance is then converted into *o*-hydroxybenzoylformic acid (3) by the aid of the diazo reaction. Reduction with sodium amalgam converts this compound into α-hydroxy-α-*o*-hydroxyphenylacetic acid, (4) which, on reduction with hydriodic acid, yields *o*-hydroxyphenylacetic acid (5)



$$\underset{(1)}{C_6H_4\!<\!\begin{smallmatrix}CO\\NH\end{smallmatrix}\!>\!CO} \rightarrow \underset{(2)}{C_6H_4\!<\!\begin{smallmatrix}CO\cdot COOH\\NH_2\end{smallmatrix}}$$

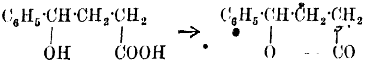
$$\rightarrow \underset{(3)}{C_6H_4\!<\!\begin{smallmatrix}CO\cdot COOH\\OH\end{smallmatrix}} \rightarrow \underset{(4)}{C_6H_4\!<\!\begin{smallmatrix}CH(OH)COOH\\OH\end{smallmatrix}}$$

$$\rightarrow \underset{(5)}{C_6H_4\!<\!\begin{smallmatrix}CH_2\cdot COOH\\OH\end{smallmatrix}}$$

Under section (*b*) may be given, as illustration, the example of γ-phenyl-γ-hydroxybutyric acid, $C_6H_5\cdot CH(OH)CH_2\cdot CH_2\cdot COOH$, which can be produced by the reduction of β-benzoylpropionic acid

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$$

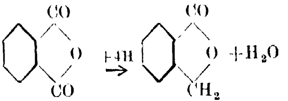
and by other methods. Although this substance is more stable than the corresponding γ-hydroxy acids of the aliphatic series, and can be isolated in the free state, it nevertheless passes into the γ-lactone when heated above its melting-point (75°).



Phenylbutyrolactone.

The hydroxy acid may be recrystallised from warm water, but at 80° lactone formation slowly occurs, and when the acid is treated with very dilute hydrochloric acid the transformation into the lactone (m.p. 37°) is complete even at low temperatures.

The γ-lactones included under section (*c*) are known as the *phthalides*, a name which is derived from that of the first member of the series, phthalide. Phthalide itself may be conveniently prepared by the reduction of phthalic anhydride

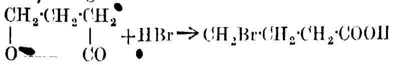


Phthalide.

Other methods of preparation will be found under the head of *Meconine* (*q.v.*).

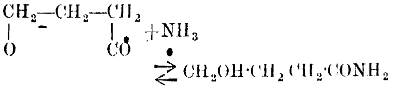
General properties of γ-lactones.—As already mentioned, the γ-hydroxy acids of the aliphatic series are, for the most part, unstable, and therefore cannot be isolated in the free state. The corresponding γ-lactone separates in almost every case when the aqueous solution of the salt of the acid is acidified even at low temperatures and in only one or two instances has it been found possible to isolate the hydroxy acid in the free condition. Thus Fittig and Chanlarow (Annalen, 1884, 226, 325, 334) found that γ-hydroxybutyric acid as well as its ethyl derivatives are stable at very low temperatures The lactones titrate as monobasic acids, and the salts of the corresponding hydroxy acid can usually be isolated in the crystalline condition ; the silver salts, which are mostly well defined crystalline substances, can be readil obtained by double decomposition from th potassium salt.

The γ-lactones derived from the mono hydroxy-mono-carboxylic acids of the aliphati series, and which therefore have the genera formula $C_nH_{2n-2}O_2$, are neutral, colourles liquids or low-melting solids which are volatil with steam, and can be distilled without de composition under ordinary atmospheric pres sure. The lower members of the series ar miscible with water in all proportions, but th solubility decreases with increase of molecula weight. The less soluble γ-lactones are fr quently characterised by possessing the curiou property of being varyingly soluble in water thus when a concentrated solution of the lacto is warmed, the solution becomes cloudy owi to the partial separation of the dissolved su stance; the emulsion again clears above 80 When the γ-lactones are dissolved in water, partial conversion into the hydroxy acid takes place, and a state of equilibrium between the two compounds is attained. Thus it has been found by P. Henry (Zeitsch. physikal. Chem. 1892, 10, 96) that a boiling 1 p.c. solution of butyrolactone contains 80 p.c. of the lactone and 20 p.c. of the hydroxy acid. γ-Lactones frequently react with halogen hydrides, yielding the γ-halogen derivatives of the acid, thus:



$$\begin{array}{lll} CH_2{\cdot}CH_2{\cdot}CH_2 & & \\ | \qquad\quad | & +HBr \rightarrow & CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \\ O \text{———} CO & & \end{array}$$

but the breaking of the lactone ring in this manner is usually more easily effected by heating the compound with an alcoholic solution of the halogen hydride, whereby the corresponding ester is formed (Henry, Compt. rend. 1886, 102, 368; Cloves, Annalen, 1901, 319, 362). When treated with aqueous ammonia in the cold, the γ-lactones yield the amide of the hydroxy acid, thus:

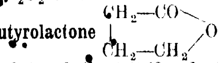


$$\begin{array}{ll} CH_2\text{—}CH_2\text{—}CH_2 & \\ | \qquad\qquad\quad | & +NH_3 \\ O \qquad\qquad\quad CO & \\ & \rightleftarrows CH_2OH{\cdot}CH_2{\cdot}CH_2{\cdot}CONH_2 \end{array}$$

These compounds readily split off ammonia and pass again into the lactone (Fittig and Rasch, Annalen, 1890, 256, 151; Fittig and Dubois, *ibid.* 1890, 256, 153). The γ-lactones react with hydrazine (Blanc and Luttringer, Bull. Soc. chim. 1905, [iii.] 33, 1095) also with potassium cyanide (Wislicenus, Annalen, 1886, 233, 113; Blanc, Bull. Soc. chim. 1905, [iii.] 33, 886, 904).

The more important γ-lactones of the formula $C_nH_{2n-2}O_2$ are:

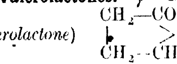
Butyrolactone



$$\begin{array}{l} CH_2\text{—}CO \\ | \qquad\quad \rangle O \\ CH_2\text{—}CH_2 \end{array}$$

Preparation method (3): boils at 204° and solidifies at −42°. It has sp.gr. 1·129 at 16°.

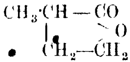
Valerolactones. γ-*Methylbutyrolactone* (*n-valerolactone*)



$$\begin{array}{l} CH_2\text{—}CO \\ | \qquad\quad \rangle O \\ CH_2\text{—}CH{\cdot}CH_3 \end{array}$$

Preparation from lævulic acid method (3); occurs in pyroligneous acid (crude acetic acid from the distillation of wood). It boils at 206°–207°, solidifies at −31°, and has sp.gr. 1·072 at 0°. The reduction of lævulic acid to the lactone is very readily effected by hydrogen at 250° (method of Sabatier and Senderens).

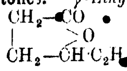
α-*Methylbutyrolactone*



$$\begin{array}{l} CH_3{\cdot}CH\text{—}CO \\ | \qquad\qquad \rangle O \\ CH_2\text{—}CH_2 \end{array}$$

is a pungent-smelling oil, boiling at 200°–202°.

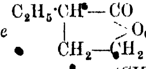
Caprolactones. γ-*Ethylbutyrolactone* (*n-caprolactone*)



$$\begin{array}{l} CH_2\text{—}CO \\ | \qquad\quad \rangle O \\ CH_2\text{—}CH{\cdot}C_2H_5 \end{array}$$

boils at 220°.

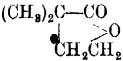
α-*Ethylbutyrolactone*



$$\begin{array}{l} C_2H_5{\cdot}CH\text{—}CO \\ | \qquad\qquad \rangle O \\ CH_2\text{—}CH_2 \end{array}$$

boils at 215°.

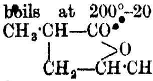
$\alpha\alpha$-*Dimethylbutyrolactone*



$$\begin{array}{l} (CH_3)_2C\text{—}CO \\ | \qquad\qquad \rangle O \\ CH_2CH_2 \end{array}$$

boils at 200°–201°.

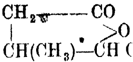
$\alpha\gamma$-*Dimethylbutyrolactone*



$$\begin{array}{l} CH_3{\cdot}CH\text{—}CO \\ | \qquad\qquad \rangle O \\ CH_2\text{—}CH{\cdot}CH_3 \end{array}$$

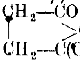
boils at 206°.

$\beta\gamma$-*Dimethylbutyrolactone*



$$\begin{array}{l} CH_2\text{———}CO \\ | \qquad\qquad\qquad \rangle O \\ CH(CH_3)\text{—}CH{\cdot}CH_3 \end{array}$$

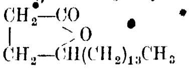
boils at 212°, and $\gamma\gamma$-*Dimethylbutyrolactone* (isocaprolactone)



$$\begin{array}{l} CH_2\text{—}CO \\ | \qquad\quad \rangle O \\ CH_2\text{—}C(CH_3)_2 \end{array}$$

boils at 95° (20 mm.), and at 206°–207° under ordinary atmospheric pressure. It melts at +6° and dissolves in 20 parts of water at 0°.

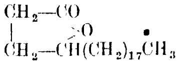
Stearolactone (γ-*tetradecylbutyrolactone*)



$$\begin{array}{l} CH_2\text{—}CO \\ | \qquad\quad \rangle O \\ CH_2\text{—}CH(CH_2)_{13}CH_3 \end{array}$$

is formed, in yield of 30–40 p.c., when oleic acid, elaidic acid, or *iso*-oleic acid is warmed with zinc chloride or concentrated sulphuric acid at 80°–85°. It crystallises from alcohol as leaflets melting at 47°–48°.

Behenolactone (γ-*octodecylbutyrolactone*)

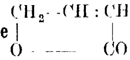


$$\begin{array}{l} CH_2\text{—}CO \\ | \qquad\quad \rangle O \\ CH_2\text{—}CH(CH_2)_{17}CH_3 \end{array}$$

which is formed from erucic acid by the action of sulphuric acid, crystallises from alcohol or ether as plates melting at 63·5°.

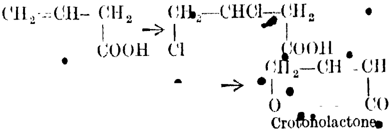
The unsaturated monohydroxymonocarboxylic acids also yield γ-lactones, and the following are important members of this series:—

Crotonolactone



$$\begin{array}{l} CH_2\text{—}CH:CH \\ | \qquad\qquad\quad | \\ O \text{———} CO \end{array}$$

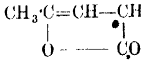
is formed from vinylacetic acid by converting it into $\beta\gamma$-dichlorobutyric acid by the addition of chlorine and then eliminating hydrogen chloride by heating at 200°–215°. It melts at 4° and boils at 95°–96° (13 mm.):



$$\begin{array}{lll} CH_2{=}CH\text{—}CH_2 & & CH_2\text{—}CHCl\text{—}CH_2 \\ \qquad\qquad | & \rightarrow & | \qquad\qquad\qquad | \\ \qquad\quad COOH & & Cl \qquad\qquad\quad COOH \\ & & \rightarrow \begin{array}{l} CH_2\text{—}CH{=}CH \\ | \qquad\qquad\quad | \\ O \text{———} CO \end{array} \end{array}$$

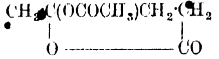
Crotonolactone.

$\Delta^{\beta\gamma}$-Angelicalactone



$$\begin{array}{l} CH_3{\cdot}C{=}CH\text{—}CH_2 \\ | \qquad\qquad\qquad | \\ O \text{———} CO \end{array}$$

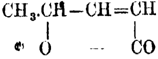
is formed, unaccompanied by the $\Delta^{\alpha\beta}$-lactone (*see* below), when acetyllævulic acid



$$\begin{array}{l} CH_2{\cdot}C(OCOCH_3)CH_2{\cdot}CH_2 \\ \quad | \qquad\qquad\qquad\qquad | \\ \quad O \text{—————} CO \end{array}$$

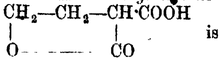
is distilled under 200–230 mm. pressure. It melts at 18°–18·5°, and distils at 55°–56° (12 mm.),

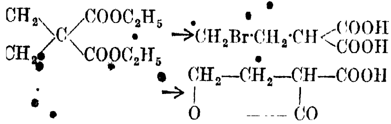
$\Delta^{\alpha\beta}$-*Angelicalactone*

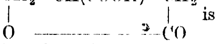


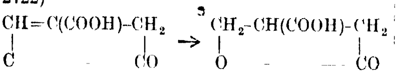
$$\begin{array}{l} CH_3.CH\text{—}CH{=}CH \\ \qquad | \qquad\qquad\quad | \\ \qquad O \text{———} CO \end{array}$$

is formed from the $\Delta^{\beta\gamma}$ compound by warming it with triethylamine. It does not solidify at −17°, and boils at 89° (15 mm.). The $\Delta^{\alpha\beta}$-lactone is partially converted into the $\Delta^{\beta\gamma}$-lactone on distillation under ordinary pressure (Thiele, Tischbein, and Lossow, Annalen, 1910, 319, 180).

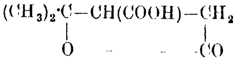
The γ-lactones which are derived from the hydroxydicarboxylic acids are, of course, no longer neutral substances, but contain a free carboxyl group; the following compounds are important members of this class: *Butyrolactone-α-carboxylic acid*  $\begin{array}{lll} CH_2—CH_2—CH\cdot COOH \\ | & & | \\ O———— & & CO \end{array}$ is formed from ethyl *cyclo*propane-1 : 1-dicarboxylate by the addition and subsequent elimination of hydrogen bromide (Fittig and Roder, Annalen, 1885, 227, 19):

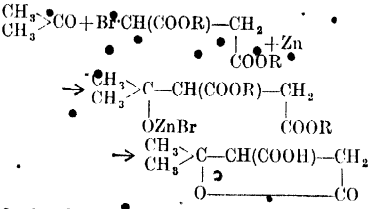

$$\begin{array}{l} \begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix} \rightarrow CH_2Br\cdot CH_2\cdot CH\!<\!\!\begin{matrix} COOH \\ COOH \end{matrix} \\ \rightarrow \begin{array}{lll} CH_2—CH_2—CH—COOH \\ | & & | \\ O & ——— & CO \end{array} \end{array}$$

The lactonic acid forms a thick viscid liquid which is readily soluble in water, and when heated at 120° evolves carbon dioxide and passes into butyrolactone. *Butyrolactone-β-carboxylic acid, Paraconic acid*  $\begin{array}{lll} CH_2—CH(COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array}$ is formed by the reduction of aconic acid by zinc-dust and acetic acid (Reitter, Ber. 1898, 31, 2722)

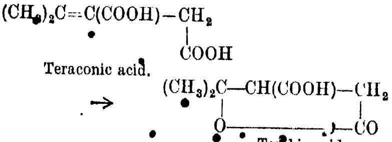

$$\begin{array}{lll} CH{=}C(COOH)\text{-}CH_2 \\ | & & | \\ C & — & CO \end{array} \rightarrow \begin{array}{lll} CH_2\text{-}CH(COOH)\text{-}CH_2 \\ | & & | \\ O & ——— & CO \end{array}$$

Aconic acid. Paraconic acid.

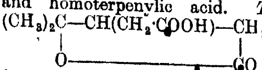
Terebic acid  $\begin{array}{lll} (CH_3)_2\cdot C—CH(COOH)—CH_2 \\ | & & | \\ O & ——— & CO \end{array}$ is a product of the oxidation of oil of turpentine, and has been synthesised by several methods. Thus it is formed by the oxidation of *iso*propylsuccinic acid, as indicated by method (5), and is also produced when the ester, formed by the condensation of ethyl bromosuccinate with acetone in the presence of zinc (Reformatzky's method), is hydrolysed:

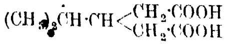

$$\begin{array}{l} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO + Br\cdot CH(COOR)—\begin{array}{l} CH_2 \\ | \\ COOR \end{array} + Zn \\ \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\begin{array}{lll} C—CH(COOR)—CH_2 \\ | & & | \\ OZnBr & & COOR \end{array} \\ \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\begin{array}{lll} C—CH(COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array} \end{array}$$

It is also obtained from teraconic acid by warming with sulphuric acid

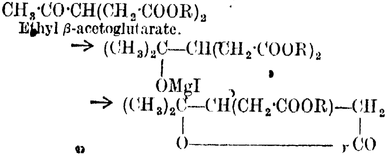

$$\begin{array}{l} (CH_3)_2C{=}C(COOH)—\begin{array}{l} CH_2 \\ | \\ COOH \end{array} \\ \text{Teraconic acid.} \\ \rightarrow \begin{array}{lll} (CH_3)_2C—CH(COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array} \\ \text{Terebic acid.} \end{array}$$

Terebic acid crystallises from water as needles which melt at 174°–175°.

Two other lactonic acids, which have played an important part in the elucidation of the chemistry of the terpenes, are terpenylic acid and homoterpenylic acid. *Terpenylic acid*  $\begin{array}{lll} (CH_3)_2C—CH(CH_2\cdot COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array}$ which occurs frequently as a product of the degradation of the terpenes, was discovered by Hempel and investigated by Fittig and his pupils; its structure was determined by Wallach. The acid has been synthetically prepared by Lawrence (Chem. Soc. Trans. 1899, 75, 529) by the oxidation of β-*iso*propylglutaric acid

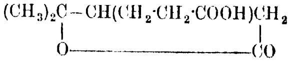

$$(CH_3)_2CH\cdot CH\!<\!\!\begin{matrix} CH_2\cdot COOH \\ CH_2\cdot COOH \end{matrix}$$

(compare method (5)), and by Simonsen (Chem. Soc. Trans. 1907, 91, 187) by the action of magnesium methyl iodide on ethyl β-acetoglutarate

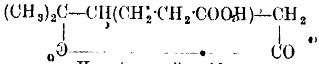

$$\begin{array}{l} CH_3\cdot CO\cdot CH(CH_2\cdot COOR)_2 \\ \text{Ethyl } \beta\text{-acetoglutarate.} \\ \rightarrow \begin{array}{l} (CH_3)_2C—CH(CH_2\cdot COOR)_2 \\ \quad | \\ \quad OMgI \end{array} \\ \rightarrow \begin{array}{lll} (CH_3)_2C—CH(CH_2\cdot COOR)—CH_2 \\ | & & | \\ O & ———— & CO \end{array} \end{array}$$

Terpenylic acid crystallises with 1 molecule of water as colourless prisms which melt at 56°. The water of crystallisation is removed by sulphuric acid and the anhydrous substance then melts at 89°.

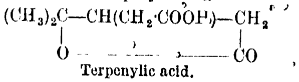
Homoterpenylic acid


$$\begin{array}{lll} (CH_3)_2C—CH(CH_2\cdot CH_2\cdot COOH)CH_2 \\ | & & | \\ O & ———— & CO \end{array}$$

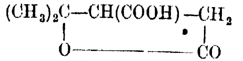
was isolated by Baeyer during his researches on the constitution of pinene—the chief constituent of oil of turpentine: its relation to terpenylic acid and terebic acid is shown by the following formulæ:—


$$\begin{array}{lll} (CH_3)_2C—CH(CH_2\cdot CH_2\cdot COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array}$$

Homoterpenylic acid.

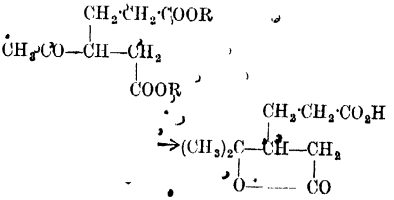

$$\begin{array}{lll} (CH_3)_2C—CH(CH_2\cdot COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array}$$

Terpenylic acid.


$$\begin{array}{lll} (CH_3)_2C—CH(COOH)—CH_2 \\ | & & | \\ O & ———— & CO \end{array}$$

Terebic acid.

Homoterpenylic acid is, as a matter of fact, converted into terpenylic acid and some terebic acid by oxidation with nitric acid. Homoterpenylic acid has been synthesised by Simonsen (Chem. Soc. Trans. 1907, 91, 184) by treating ethyl β-acetoadipate with magnesium methyl iodide and hydrolysing the product.


$$\begin{array}{l} \begin{array}{lll} & CH_2\cdot CH_2\cdot COOR \\ & | \\ CH_3\cdot CO—CH—CH_2 \\ & & | \\ & & COOR \end{array} \\ \rightarrow \begin{array}{lll} & CH_2\cdot CH_2\cdot CO_2H \\ & | \\ (CH_3)_2C—CH—CH_2 \\ | & & | \\ O & —— & CO \end{array} \end{array}$$

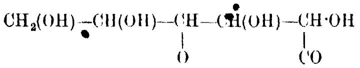
The acid crystallises from water as glistening prisms which melt at 100°–102°.

The formation of γ-lactones from polyhydroxy-carboxylic acids. Those polyhydroxy derivatives of the carboxylic acids which have a hydroxyl group in the γ-position yield γ-lactones (Fittig, Annalen, 1892, 268, 4, 34, 40, 62, 68).

When hydroxyl groups are present in both the γ- and δ- positions, the γ-lactone is formed, since the five-membered γ-lactone ring is more easily closed than the six-membered δ-lactone ring, thus:

$$CH_2(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}CH(OH)\text{-}COOH$$

Gluconic acid.



$$CH_2(OH)-CH(OH)-\underset{\substack{|\\ O}}{CH}-CH(OH)-\underset{\substack{|\\ CO}}{CH\cdot OH}$$

Gluconolactone.

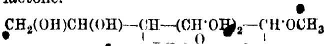
The hydroxylactones, which are derived from the acids of the sugar group and which therefore contain several hydroxyl complexes, are characterised by showing a greater tendency to crystallise than the hydroxy acids themselves; their formation has therefore been of considerable service in elucidating the structure of the sugars. The remarkable property possessed by the acids of the sugar group of passing into the aldehyde, that is, the sugar itself, when reduced by nascent hydrogen, thus:

$$\underset{\text{Gluconic acid.}}{CH_2(OH)-(CH\cdot OH)_4-COOH} \rightarrow \underset{\text{Glucose.}}{CH_2(OH)(CH\cdot OH)_4CHO}$$

is entirely dependent on the formation of the lactone. That is to say, the acid itself is not reducible but only the lactone (E. Fischer, Ber. 1889, 22, 2204; 1890, 23, 930).

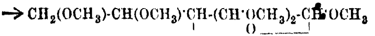
The following lactones are derived from the pentahydroxycarboxylic acids: *d-Mannonolactone* $C_6H_{10}O_6$ melts at 149°–153°, and has $[\alpha]_D = +53\cdot8°$; *l-Mannonolactone* melts at 140°–150°, and has $[\alpha]_D = -54\cdot8°$; *(d+l)-Mannonolactone* melts at 149°–155°. *d-Gluconolactone* $C_6H_{10}O_6$ melts at 130°–135° and yields grape sugar when reduced by sodium amalgam. *l-Gluconolactone* melts at 185° and gives *l*-xylose when oxidised by hydrogen peroxide. *d-Galactonolactone* melts at 91° in the anhydrous state, but with water yields a hydrate, containing one molecule of water of crystallisation, which melts at 61°. The *(d+l)-lactone* melts at 122°–125°. α-*Rhamnoselactone* melts at 162°–168°; β-*Rhamnoselactone* melts at 134°–138°. The following lactones are derived from the hexahydroxycarboxylic acids: *d-Mannoselactone* (m.p. 149°); *l-Mannoselactone* (m.p. 154°); α-*d-Glucoselactone* (m.p. 140°–145°); β-*d-Glucoselactone* (m.p. 151°); α-*d-Galactoselactone* (m.p. 150°); *d-Fructoselactone* (m.p. 130°). These lactones are reduced by sodium amalgam to the corresponding heptoses.

The formation of γ-lactones from the acids of the sugar series has been used by Purdie and Irvine (Chem. Soc. Trans. 1903, 83, 1021) to supply direct evidence of the γ- linkage in glucosides. Thus α-methylglucoside when alkylated by the aid of silver oxide yields tetramethyl-α-methylglucoside which, on hydrolysis, is converted into tetramethylglucose (m.p. 81°–83°). When this substance is oxidised by bromine water it is converted into tetramethylgluconolactone.



$$CH_2(OH)CH(OH)-\underset{|}{CH}-(CH\cdot OH)_2-\underset{|}{CH}\cdot OCH_3 \quad (\text{bridged by } O)$$

α-Methylglucoside.



$$\rightarrow CH_2(OCH_3)\text{-}CH(OCH_3)\cdot\underset{|}{CH}\text{-}(CH\cdot OCH_3)_2\text{-}\underset{|}{CH}\cdot OCH_3$$

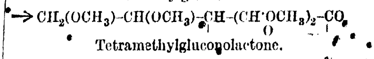
Tetramethyl-α-methylglucoside.

$$\rightarrow CH_2(OCH_3)\text{-}CH(OCH_3)\text{-}CH(OH)\text{-}(CH\cdot OCH_3)_2CHO$$

Tetramethylglucose (m.p. 81°–83°).

$$CH_2(OCH_3)\text{-}CH(OCH_3)\text{-}CH(OH)\text{-}(CH\cdot OCH_3)_2\text{-}COOH$$

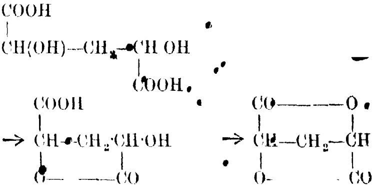
Tetramethylgluconic acid.



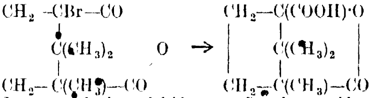
$$\rightarrow CH_2(OCH_3)\text{-}CH(OCH_3)\text{-}\underset{|}{CH}\text{-}(CH\cdot OCH_3)_2\text{-}\underset{|}{CO}$$

Tetramethylgluconolactone.

Polyhydroxy derivatives of the dicarboxylic acids yield γγ-dilactones, where possible. Thus αα′-dihydroxyglutaric acid yields in the first instance the hydroxylactonic acid melting at 167°–168°, and finally the dilactone (Fittig, Annalen, 1907, 353, 1)

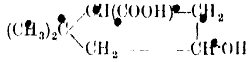


The formation of lactones from alicyclic compounds appears to proceed in much the same manner as with the open chain substances. In many cases, the formation of the lactone proceeds normally as, for example, when bromocamphoric anhydride is converted into camphanic acid by the action of boiling water (Wreden, Annalen, 1872, 163, 330):



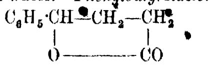
Bromocamphoric anhydride. Camphanic acid.

On the other hand, steric hindrance seems, in some cases, to prevent the formation of the lactone. Thus 1-1-dimethyl-4-hydroxy-*cyclo*pentane-2-carboxylic acid



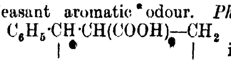
shows no tendency to pass into the inner anhydride (Perkin, Thorpe, and Walker, Trans. 1901, 79, 783). It is, however, possible that in this instance the hydroxy acid may represent the *trans*-configuration of this substance, in which case the formation of the lactone would be prevented (*see* orthocoumaric acid).

The γ-lactones of the aromatic series. The following lactones are important members of this series. (For methods of preparation see above.) *The lactone of o-hydroxyphenylacetic acid* $C_6H_4\langle\begin{smallmatrix}CH_2\\ O\end{smallmatrix}\rangle CO$, exists in two modifications, a labile form, melting at 28°, and a stable form, melting at 49°. It boils at 248°–252° and is slowly converted into the hydroxy acid on shaking with water. *Phenylbutyrolactone*



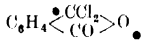
$$C_6H_5\cdot\underset{\substack{|\\ O}}{CH}-CH_2-\underset{\substack{|\\ CO}}{CH_2}$$

melts at 37°. It is volatile with steam and has a pleasant aromatic odour. *Phenylparaconic acid*



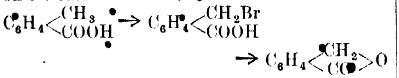
$$C_6H_5\cdot\underset{\substack{|\\ O}}{CH}\cdot CH(COOH)-\underset{\substack{|\\ CO}}{CH_2}$$

is formed by the condensation of benzaldehyde with sodium succinate in the presence of acetic anhydride. It crystallises with $\frac{1}{2}H_2O$ and melts at 99°. When dried at 90° it melts at 121° and after resolidifying melts at 106°. If the melted specimen is heated at 115° and seeded with a crystal melting at 121°, the modification of higher melting-point is produced (Fittig, Annalen, 1889, 255, 143). It is sparingly soluble in cold water. *Phthalide* $C_6H_4<\substack{CO \\ CH_2}>O$ is formed by the reduction of phthalic anhydride and was first obtained by Kolbe and Wischin in 1866 by the reduction of phthalyl chloride



$$C_6H_4<\substack{CCl_2 \\ CO}>O$$

It can also be obtained by the action of bromine on *o*-toluic acid at 140°



$$C_6H_4<\substack{CH_3 \\ COOH} \rightarrow C_6H_4<\substack{CH_2Br \\ COOH}$$

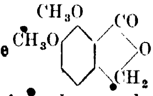
$$\rightarrow C_6H_4<\substack{CH_2 \\ CO}>O$$

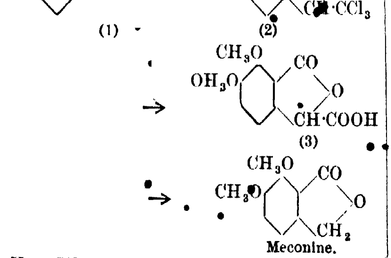
Phthalide.

Phthalide crystallises from hot water as rhombic plates which melt at 73°; it boils at 290° without decomposition and is sparingly soluble in alcohol, ether and in cold water. The lactone is converted by alkalis into the salt of the corresponding hydroxy acid

$$C_6H_4(CH_2{\cdot}OH)COOH$$

This acid is stable, but by long standing in aqueous solution, or by melting, is converted into phthalide.

Meconine  This substance, which was formerly named *opianyl*, was discovered independently in 1830 by Couerbe and by Dublanc in opium. It also occurs in the root of the *Hydrastis canadensis* (Linn.), and is, moreover, one of the products which are formed when narcotine is oxidised by nitric acid. It has been prepared synthetically by Fritsch in the following way (Annalen, 1898, 301, 352): Methyl 2:3-dimethoxybenzoate (1) is condensed with chloral, under the influence of concentrated sulphuric acid, to form 5:6-dimethoxytrichloromethylphthalide. (2) This compound, when hydrolysed, is converted into the corresponding carboxylic acid, (3) which is transformed into carbon dioxide and meconine when heated:

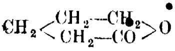


Meconine.

Meconine forms white crystals which melt at 101°–102°. It sublimes unchanged and dissolves in 700 parts of water at 15·5° and in 22 parts at 100°.

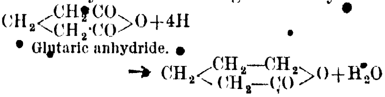
δ-Lactones. The remarks which have already been made respecting the case of formation of the γ-lactones from the γ-hydroxy acids apply also to the production of the δ-lactones from the corresponding δ-hydroxy acids, excepting that the six-membered δ-lactone ring is not so readily formed as the five-membered ring of the γ-lactones and is consequently more easily broken.

Aliphatic δ-lactones. δ-*Valerolactone*



$$CH_2<\substack{CH_2{-}CH_2 \\ CH_2{-}CO}>O$$

is formed by the reduction of glutaric anhydride:

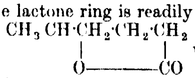


$$CH_2<\substack{CH_2{\cdot}CO \\ CH_2{\cdot}CO}>O+4H$$

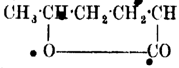
Glutaric anhydride.

$$\rightarrow CH_2<\substack{CH_2{-}CH_2 \\ CH_2{-}CO}>O+H_2O$$

It boils at 113°–114° (13–14 mm.) and at 220° under ordinary atmospheric pressure, is sparingly soluble in water and is characterised by passing, on standing, into a crystalline polymeride melting at 47°–48°. When water is added to the lactone an acid reaction is at once obtained, showing that the lactone ring is readily broken.

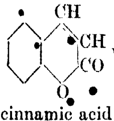
δ-*Caprolactone*,  was the first δ-lactone of the aliphatic series to be prepared, and was obtained by Fittig and Wolff (Annalen, 1883, 216, 127) by the reduction of γ-acetobutyric acid:

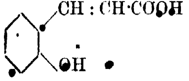
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$$



It boils at 230°–231° and forms needles melting at 17°–19°. It is miscible with water and absorbs moisture from damp air, passing into the hydroxy acid.

Aromatic δ-lactones. Several δ-lactones of the aromatic series are of considerable importance because they either occur free in nature or are obtained as the products of fission of certain natural glucosides. They are largely used industrially for the preparation of perfumes.

Coumarin  which is the δ-lactone of *o*-hydroxycinnamic acid



may be regarded as the prototype of this group to which the general name of 'the Coumarins' is applied, chiefly because the other members of the series are derivatives of coumarin in which hydroxyl or methoxyl groups are present in the benzene nucleus.

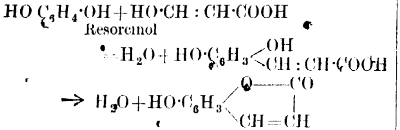
The coumarins may be prepared either by applying the Perkin method for the synthesis of coumarin (see below) to the necessary derivatives of salicylaldehyde, or by the v. Pechmann method, which is carried out by heating phenols with malic acid in the presence of concentrated sulphuric acid (v. Pechmann, Ber. 1884, 17, 929; v. Pechmann and Welsch, *ibid.* 1646). This reaction is explained by assuming that the strong sulphuric acid first decomposes malic acid into carbon monoxide, water, and hydroxyacrylic acid, thus:

$$COOH\cdot CH(OH)CH_2\cdot COOH$$

Malic acid.

$$\rightarrow CO + H_2O + CH(OH):CH\cdot COOH$$

and that the hydroxyacrylic acid then condenses with the phenol to form the coumarin, thus:



$$HO\cdot C_6H_4\cdot OH + HO\cdot CH:CH\cdot COOH$$

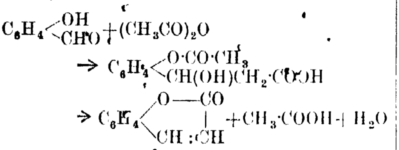
Resorcinol

$$= H_2O + HO\cdot C_6H_3\lt\begin{array}{l}OH\\CH:CH\cdot COOH\end{array}$$

$$\rightarrow H_2O + HO\cdot C_6H_3\lt\begin{array}{l}O\text{——}CO\\ \qquad\quad |\\CH=CH\end{array}$$

Umbelliferone.

This reaction yields the best results with the *m*-substitutes phenols. *Coumarin* was first isolated in 1820 from Tonka beans, the seed of the *Dipteryx odorata* (Willd.), and was subsequently characterised by Guibort. It was first prepared synthetically by Perkin from salicylaldehyde by heating with sodium acetate and acetic anhydride:



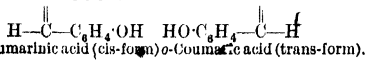
$$C_6H_4\lt\begin{array}{l}OH\\CHO\end{array} + (CH_3CO)_2O$$

$$\rightarrow C_6H_4\lt\begin{array}{l}O\cdot CO\cdot CH_3\\CH(OH)CH_2\cdot COOH\end{array}$$

$$\rightarrow C_6H_4\lt\begin{array}{l}O\text{——}CO\\ \qquad\quad |\\CH:CH\end{array} + CH_3\cdot COOH + H_2O$$

This synthesis may, moreover, be applied to the formation of other coumarins since, by the method of Gattermann (Ber. 1899, 32, 278, 287), many hydroxyaromatic aldehydes can now be prepared from phenols by the action of hydrocyanic and hydrochloric acids in the presence of aluminium chloride.

Coumarin forms prismatic crystals which melt at 67° and boil at 290°–290·5°. It is sparingly soluble in cold water but readily dissolves on warming. The corresponding hydroxy acid, coumarinic acid, cannot be isolated in the free state, but when coumarin is boiled for some time with a solution of potassium hydroxide, an acid separates on acidification which decomposes above 200° with evolution of carbon dioxide but does not yield coumarin (Zwenger, Annalen Suppl. 1872, 8, 23). This acid, which is called orthocoumaric acid, is stereoisomeric with the unstable coumarinic acid (Clayton, Chem. Soc. Trans. 1910, 2102) the two acids being represented by the formulæ:

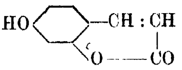


$$\begin{array}{c}H\text{—}C\text{—}COOH\\ \|\\ H\text{—}C\text{—}C_6H_4\cdot OH\end{array}\qquad\begin{array}{c}H\text{—}C\text{—}COOH\\ \|\\ HO\cdot C_6H_4\text{—}C\text{—}H\end{array}$$

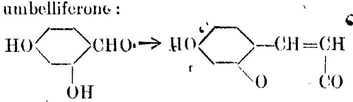
Coumarinic acid (cis-form) *o*-Coumaric acid (trans-form).

The ease of formation of coumarin from coumarinic acid is explained by the proximity of the hydroxyl and carboxyl groups in the cis-configuration (*cf.* Borsche, Ber. 1904, 37, 346).

Umbelliferone, Hydroxycoumarin



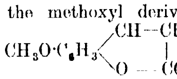
This substance, which is the δ-lactone of 2 : 4-dihydroxycinnamic acid, is found in the bark of the *Daphne Mezereum* (Linn.) and is also obtained by distilling various resins such as galbanum and asafœtida. Its synthesis may be effected directly from resorcinol by v. Pechmann's malic acid method, or indirectly from resorcylaldehyde by the aid of Perkin's reaction, a method which establishes the position of the hydroxyl group in umbelliferone:



Resorcylaldehyde. Umbelliferone.

Umbelliferone crystallises from hot water in slender needles melting at 225°. It dissolves very sparingly in water, yielding a solution which shows a marked blue fluorescence.

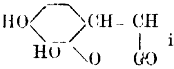
Herniarin is the methoxyl derivative of umbelliferone



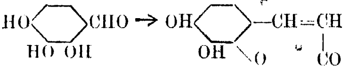
$$CH_3O\cdot C_6H_3\lt\begin{array}{l}CH\text{—}CH\\ \qquad\ |\\O\text{——}CO\end{array},$$

and occurs in *Herniaria hirsuta* (Linn.) (Barth and Herzig, Monatsh. 1889, 10, 161). It melts at 117°–118°.

Daphnetin



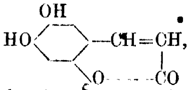
is obtained by the fission of the glucoside daphnin, either by acids or by ferments. It can be prepared synthetically either from pyrogallol by the malic acid method or from pyrogallolaldehyde by Perkin's reaction; the second method of preparation determines the positions of the hydroxyl groups in daphnetin:



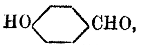
Pyrogallolaldehyde. Daphnetin.

Daphnetin crystallises as needles or prisms, melts at 256°, and develops a pleasant coumarin-like smell when heated. It dissolves in alkali, forming a reddish-yellow solution and gives in aqueous solution a green coloration with ferric chloride.

Æsculetin

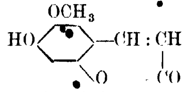


is isomeric with daphnetin. It occurs in the bark of the horse chestnut, partly free and partly as the glucoside æsculin. It also occurs in the seed of the *Euphorbia Lathyris* (Linn.), and can be prepared synthetically from hydroxyhydroquinone by converting this substance into hydroxyhydroquinonealdehyde



by means of hydrocyanic and hydrochloric acids in the presence of zinc chloride (Gattermann's reaction), and then by subjecting the aldehyde to the Perkin reaction. Æsculetin crystallises from water as leaflets or needles, melts at 268° with decomposition, and is sparingly soluble in cold water, but readily dissolves in hot water and in alcohol. The aqueous solution, which has a faint blue fluorescence gives a green coloration with ferric chloride The lactone dissolves in alkali, forming a yellowish-red solution.

Scopoletin (*Chrysatropic acid*)

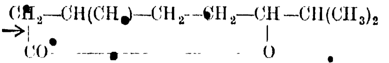


which is the methoxyl derivative of æsculetin, was isolated by Eykman (Rec. trav. chim. 1884, 3, 171) from the rhizome of *Scopolia japonica* (Maxim.). It also occurs in *Atropa belladonna* (Linn.), in *Gelsemium*, in the bark of the *Prunus serotina*, and in jalap. The lactone crystallises from ethyl acetate as needles which melt at 204°, and exhibits a fine blue fluorescence in aqueous solution, which is enhanced by the addition of alkali. The constitution of this substance as 4-hydroxy-5-methoxy-coumarin has been determined by Moore (Chem. Soc. Trans. 1911, 99, 1043).

ε-Lactones. The existence of ε-lactones has been shown to be possible by the researches of v. Baeyer and his collaborators. Thus when the hydroxy acid (1) is distilled, it is partially decomposed into water and the ε-lactone: β-methyl-ε-*iso*propyl-ε-caprolactone (2) (Baeyer and Öhler, Ber. 1896, 29, 29; Baeyer and Seuffert, *ibid.* 1899, 32, 3619):

$$COOH{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH_2{\cdot}CH(OH)CH(CH_3)$$

(1)

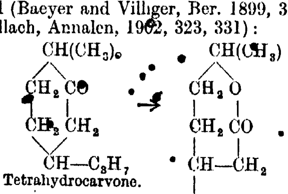


$$\rightarrow \begin{array}{l} CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}CH{-}CH(CH_3)_2 \\ CO \text{---------------------} O \end{array}$$

(2)

The hydroxy acid (1), which is derived from menthone by oxidation and subsequent reduction, exists in two forms, one of which is liquid, the other solid. There are, therefore, two lactones (both of which are feebly lævorotatory), one melting at 47° derived from the solid acid, and the other, a liquid boiling at 135° (12 mm.) derived from the liquid acid. Both modifications of the lactone are insoluble in cold alkali but dissolve on warming. The solid ε-lactone (m.p. 47°) is also formed when menthone is oxidised by Caro's acid (Baeyer and Villiger, Ber. 1899, 32, 3628; 1900, 33, 860).

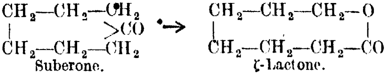
β-iso-**Propyl-ε-methyl-ε-caprolactone** is formed when tetrahydrocarvone is treated with Caro's acid (Baeyer and Villiger, Ber. 1899, 32, 3629; Wallach, Annalen, 1902, 323, 331):



Tetrahydrocarvone. ε-Lactone.

The lactone boils at 155·5° (24 mm.).

ζ-Lactones. An unstable lactone of this series is formed when suberone is treated with Caro's acid (Baeyer and Villiger, Ber. 1900, 33, 862; v. Braun, *ibid.* 1906, 39, 4362):



Suberone. ζ-Lactone.

The lactone was not isolated, but its existence in the crude product of oxidation was inferred from the fact that when treated with alcohol and sulphuric acid it was converted into the ethyl salt of ζ-hydroxyœnanthylic acid

$$OH(CH_2)_6COOR$$

J. F. T.

LACTOPHENIN *v.* SYNTHETIC DRUGS.

LACTOSE *v.* CARBOHYDRATES.

LACTUCARIUM. *Lettuce opium.* The inspissated juice of *Lactuca virosa* (Linn.) (*Lactucarium*, U.S.P.), and other species of *Lactuca* (*v.* Woodville, Med. Bot 1, 31; Bentl. a. Trim. 160, 161). Lactucarium is sometimes employed in medicine as a substitute for opium, and has often been examined chemically.

Half the weight of lactucarium, or more, consists of the tasteless inodorous compound *lactucerin* or *lactucon*, first obtained in a crystalline form by Lenoir (Annalen, 59, 83). It has been repeatedly investigated, with varying results, apparently last by Pomeranz and Sperling (Monatsh. 1904, 25, 785), who by extraction of *Lactucarium germanicum* (from *L. virosa*) with light petroleum obtained *lactucon* (=*lactucerin*) $C_{23}H_{36}O_2$, needles m.p. 183°, $[\alpha]_D^{18°} +50°$, readily soluble in most organic solvents and hot alcohol, but not in water. It is the acetate of *lacticol* $C_{21}H_{34}O$, m.p. 154·5°.

French lactucarium (from *L. virosa* or *L. altissima*) has been examined by Franchimont and Wigman (Ber. 1879, 12, 10), who obtained a lactucon which may or may not be identical with that above-mentioned. The bitter taste, and probably the medicinal properties of lactucarium, are, however, due to small quantities of *lactucin* $C_{11}H_{12}O_3,H_2O$, crystallising from hot water (Kromeyer, Arch. Pharm. 1861, 105, 3), and possibly to other substances. For the rest (German) lactucarium contains 8–10 p.c. of inorganic matter, 2 p.c. of mannitol, free oxalic acid (up to 1 p.c.), citric and malic acids, sugar, gum, asparagin, protein, caoutchouc, and resin (Kremel, Pharm. Zentralh, 1888, 512).

For *L. canadensis*, see Flowers (Pharm. J. [iii] 10, 44). G. B.

LACTUCERIN, LACTUCIN, LACTUCOL, and **LACTUCON** *v.* LACTUCARIUM.

LAC VARNISH *v.* VARNISH.

LADANUM, is a resinous exudation of Cistus *Spp.*, more particularly of *Cistus creticus*. It is dark brown in colour, softens readily when worked in the fingers, and has a peculiar pleasant odour, with a balsamic, bitter, pungent taste. Partially soluble in ether, chloroform, and alcohol, practically insoluble in water or light petroleum. Consists of a brown resin, an essential oil, and a solid crystalline substance, *ladaniol* $C_{17}H_{30}O$, m.p. 89°, resembling champacol and guaiol. The portion of ladanum insoluble in ether and alcohol contains a bassorin-like gum, which gives mucic acid on oxidation with nitric acid; a greyish-white, pulverulent resin; and a bitter substance (Emmanuel, Arch. Pharm. 1912, 250, 111).

LÆVOBORNEOL *v.* Camphors.

LÆVOCAMPHOR *v.* Camphors.

LÆVULIC ACID *v.* Ketones.

LÆVULOSE *v.* Carbohydrates.

LAKE ORE *v.* Limonite; Iron.

LAKES. The origin of their manufacture, as well as of the term 'lake' itself, is seen from the following brief historical sketch:—

According to Pliny, the dried scum collected by the dyers of Tyrian purple from their dye-liquors furnished a costly purple-coloured pigment employed by painters. The *indicum* of the Roman artists was probably obtained in the same manner from a woad or indigo vat. Caneparius, a Venetian writer on dyeing, in 1619, states that it was the custom of dyers to evaporate the waste lac dye-liquors in order to obtain an artificial lac used by artists.

Similar pigments were afterwards prepared or collected from the waste dye-liquors of kermes, brazilwood, &c. Such pigments were called by the Italians *laccæ*, and these were distinguished from each other by adding the name of the substance whence the colour was derived—*e.g. lacca di verzino* (Brazilwood), *lacca di grana* (kermes), *lacca di cremise*, &c.

As to the word 'lake' itself, the Indian 'lac' or 'lakh' means a hundred thousand, and refers to the immense numbers in which the lac insects (*Coccus laccæ*) appear at certain seasons on the branches of the trees infested with them.

At the present time true lakes are like those of the early days—namely, insoluble pigments obtained by precipitating solutions of organic colouring matters with metallic salts, &c. They are, indeed, the same coloured precipitates which it is the object of the dyer to produce and fix directly on the fibre, but they are no longer the waste products of the dye-bath, but are specially prepared for the use of artists and others.

The precipitating agent employed in their preparation varies according to the nature of the colouring matter; if the latter is of an acid or phenolic character the active constituent of the former is of a basic character, and *vice versâ*. The essential part of all such lakes consists of colouring matter chemically combined with the active constituent of the precipitating agent. In some cases, no doubt, there may be colouring matter or precipitating agent mechanically mixed with the true lake, the amount varying according to the proportions and the method of preparation adopted; but these must be regarded as more or less adventitious and not essential to the composition of a lake

Most of the vegetable colouring matters are of a phenolic character, and the metallic compounds of some are so insoluble that, to produce lakes from them, it suffices to add to a filtered solution of the colouring matter the solution of the metallic salt, for example, alum. In most cases, however, the acid character of the colouring matter is not sufficiently pronounced to enable it to displace the acid of the metallic salt; hence the further addition of an alkali (*e.g.* sodium carbonate) is necessary, in order to neutralise the strong acid of the salt and to liberate the base, with which the colouring matter then combines to form the lake.

If it is possible to employ an alkaline solution of the colouring matter, a lake may be at once obtained on adding to it a metallic salt solution.

Freshly precipitated metallic hydroxides are also capable, in many cases, of attracting and combining with phenolic colouring matters when agitated or heated with their solutions.

It is well to bear in mind that not unfrequently the normal compounds of a colouring matter with a single metallic hydroxide are comparatively soluble, and in these cases the addition of a second metallic salt (*e.g.* calcium salts) may be found necessary to bring about the formation of the lake, which then bears the character of a double salt. All the older lakes, derived from vegetable or animal colouring matters, were produced by one or other of the foregoing methods; and these same methods may be employed with all phenolic colouring matters produced from coal tar. A variety of pigments are now obtained by precipitating certain basic and acid coal tar colours from their solutions by making suitable additions, and although they are not always veritable lakes, they usually bear the name 'aniline lakes,' and are, therefore, most conveniently considered here.

In some cases, no doubt, certain elements of the precipitant combine with the colouring matter, and produce an insoluble pigment to which the term 'lake' may be legitimately extended. In those instances, however, where their production depends upon the property, possessed by many insoluble bodies, of attracting the colouring matters from their aqueous solutions by mere absorption, or in virtue of molecular surface attraction, &c., they cannot be regarded as true lakes. The same remarks apply to the modern pigments from insoluble azo colours (pigment colouring matters) and the developed or ice colours.

Such insoluble substances as are here referred to act as a base or substratum for the colouring matter; they are termed 'carriers,' and consist of kaolin, aluminium hydroxide, barytes, &c.

It is quite usual, however, to find such insoluble bodies mixed with all lakes, not as precipitants, but for the purpose of increasing the body or covering power of the pigment, or as diluents in order to obtain pale shades.

Good lakes should never dissolve in the vehicles by means of which they are applied as pigments, otherwise all their covering power will be lost, and what should be a paint becomes in this case merely a coloured varnish.

LAKES DERIVED FROM PHENOLIC COLOURING MATTERS.

Reds.

Madder-lake. In the preparation of madder-lake extraction of the madder with *boiling* water is avoided, in order not to dissolve those impurities which would cause the production of a less brilliant lake. It is well, first of all, to decompose the glucoside of the madder, and thus increase the actual colouring matter, by steeping in slightly tepid water and allowing the mixture to ferment for 24 hours, then wash with cold water and extract with alum solution at 60°–70°, employing about equal weights of madder and alum. The hot filtered alum solution of the colouring matter is precipitated as an alumina lake by adding sodium carbonate, and the precipitate is washed.

Another method is to precipitate impurities from a hot filtered decoction of madder by adding a small quantity of lead acetate, then filter, add a solution of alum, and precipitate with sodium carbonate.

Matters may be so arranged as to precipitate basic aluminium sulphate instead of aluminium hydroxide, namely, by adding an insufficiency of sodium carbonate to the cooled solution of alum and colouring matter, and then boiling the mixture.

Garancine is preferable to madder for preparing madder-lake, since it does not contain any of the colouring matter in the form of glucoside (ruberythric acid), and the soluble impurities have also been for the most part removed. Extract 1 kilo. garancine repeatedly for several hours with 20 litres of boiling water containing 0·25–0·5 kilo. alum, and filter hot through flannel. On cooling, the colouring matter separates from the filtrate as a flocculent precipitate. This is collected and dissolved in ammonia, and the filtered solution is precipitated with alum, or stannous chloride, or a mixture of both. The colour intensity of the lake varies with the proportions of ammonia and precipitant employed. A method similar to that described for madder may also be employed in preparing madder-lake from garancine.

Bright carmine-red lakes are obtained if, in the preparation of madder-lake, an ammoniacal solution of cochineal-carmine is employed for precipitating the alum solution, instead of the sodium carbonate. This method can be adopted to render the lower qualities of madder-lakes more attractive. Cheap qualities of madder-lakes are also prepared sometimes by extracting mixtures of madder and Brazilwood with sodium carbonate, and precipitating with alum or a solution of tin.

So-called 'crystallised-madder-lakes' are such as contain a certain quantity of potassium or sodium sulphate, &c., and are not to be recommended.

'Madder-pink-lake' is simply madder-lake diluted with about 7 parts of 'blanc fixe' (precipitated barium sulphate).

Madder-lake is entirely, or for the most part, soluble in caustic potash and soda. If chalk or other diluent is present, this may remain undissolved. Boiled with dilute sulphuric or hydrochloric acid, the lake is decomposed, alizarin being liberated in the form of a flocculent or crystalline precipitate. In dilute ammonia pure well-made madder-lake is not soluble (distinguishing test from cochineal-carmine).

References.—Colomb, Bull. Mülh. 12, 307; Dingl. poly. J. 73, 47; Persoz, Traité de l'Impression des Tissus, 1, 507; Merimé, *ibid.* 1, 505; Robiquet and Colin, *ibid.* 1, 505; Khittel, Polyt. Centr. 1859, 81.

Alizarin-red lake is the modern representative of the old madder-lake. It is made either with alizarin (20 p.c.) only, or with mixtures of alizarin and purpurin. Generally the alizarin red lake contains, in addition to alizarin and aluminium hydroxide, calcium salts, sulphated oil (Turkey-red oil), and sodium phosphate; the exact function of these latter in the formation of the lake is not properly understood, but they exercise great influence on the brightness of the final product as well as in rendering it less sensitive to the action of dilute acids and alkalis.

The Turkey-red oil may be assumed to influence the brilliancy of the shade as in the production of Turkey red by the dyer; the part played by the sodium phosphate is more obscure, but it is always present in the finished lake, and without it there is a loss in brightness.

The absence of calcium salts is also detrimental; in most cases no satisfactory lake can then be obtained.

The general procedure is to dissolve the alizarin in a cold solution of soda, adding in succession the sodium phosphate and Turkey-red oil with thorough stirring to ensure complete admixture. The solution of aluminium sulphate is then run in at such a rate that the evolution of carbon dioxide never becomes very vigorous. When no more gas is given off the requisite amount of lime-water is included and the whole mass stirred for many hours; heat is applied very gradually, so that the boiling-point is reached in 4 or 5 hours, always stirring. After boiling for several hours the lake is allowed to cool, well washed by decantation, filtered, and dried at the temperature of the air.

A method given by Meister, Lucius, and Brüning for their brands of alizarin RR and 1B extra, is as follows:—

2 kilos. aluminium sulphate 18 p.c. are dissolved in 13 litres of water and precipitated hot by the addition of a solution of sodium carbonate (1 kilo. calcined soda in 7 litres of water), stirring continuously. The precipitated alumina is boiled for half an hour to remove the last traces of carbon dioxide, and after standing overnight, the supernatant liquor is decanted off.

To this cold substratum the solution of sodium phosphate (0·16 kilo. in 1·8 litres water) is next added, and subsequently calcium chloride (1·266 kilos. liquor, 24°Bé., diluted with 2 litres of water) in the same manner, stirring well during the additions, and taking care that the former has been thoroughly incorporated before proceeding with the latter.

2 kilos. of the colouring matter mixed with 2 litres of water and 0·6 kilo. of Turkey-red oil (50 p.c.) diluted with 0·8 litre of water are further run in with the same precautions and the whole heated gradually to boiling within 1 hour and boiled for 2½ hours, stirring throughout the whole time as before.

Modern improvements in the methods of manufacturing alizarin-red lakes have furnished results showing a much higher degree of intensity and brightness than was formerly possible. After-treatment of the lake by boiling (steaming) under pressure is said to yield brilliant shades and of great intensity.

Slight additions of tin salts are also added on occasion to brighten the shade.

In making alizarin-red lake it is very essential that the aluminium sulphate employed be free from iron if brilliant lakes are desired. Further, the solutions should be as dilute as possible, as this ensures fineness of structure and softness in the finished article.

Maroon and **claret-red lakes** are produced from alizarin with chromium salts, and **purple lakes** may be obtained by the aid of iron salts.

In connection with the production of

alizarin-red lake, the following observations of Liechti and Suida (Mittheil. Gewerb. Museum, Wien, May, 1885) are of interest.

Pure aluminium hydroxide is incapable of directly forming a lake with alizarin—*e.g.* when boiled with an aqueous solution of the latter. The addition, however, of calcium salts at once effects the formation of a lake.

Aluminium-alizarin lakes of definite composition are best prepared by mixing solutions of aluminium salts with an alkaline solution of alizarin. Lakes are also produced if a solution of aluminium acetate mixed with alizarin is heated; or if aluminium hydroxide is heated with alizarin and ammonia, and the mixture is carefully neutralised with acetic acid; or if a mixture of aluminium hydroxide, alizarin, and concentrated sodium acetate solution is heated.

Normal aluminium alizarate $Al_2(C_{14}H_6O_4)_3$, produced by the double decomposition of solutions of aluminium sulphate and ammoniacal alizarin (1 mol. Al_2O_3 to 3 mols. alizarin), forms a purplish-red precipitate, which changes to purplish-black on drying. It is soluble in distilled water and alcohol with a red colour, and in alkalis, especially ammonia, with a fine purplish-red tint. Basic aluminium alizarates of definite composition are prepared by proportionately decreasing the amount of alizarin employed in the above-mentioned decomposition.

$Al_4(C_{14}H_6O_4)_3(OH)_6$ is a bright-red precipitate changing to brownish-red on drying. It is soluble in ammonia with a bright-red colour. $Al_2(C_{14}H_6O_4)(OH)_4$ is also a bright-red precipitate, which gives a red powder on drying. In ammonia it is much less soluble than the foregoing. $Al_4(C_{14}H_6O_4)(OH)_{6}$ is a bright-red precipitate, which still remains a fiery-red powder on drying and is very sparingly soluble in ammonia. All the above basic aluminium alizarates are insoluble in water and in alcohol.

Alkaline solutions of normal aluminium alizarate and of the basic compound

$$Al_4(C_{14}H_6O_4)_3(OH)_6$$

may be mixed with solutions of sodium phosphate, sulphated oil, soap, &c., without undergoing decomposition, but, on neutralising these mixed solutions with acids, very brilliant red lakes are precipitated. Normal aluminium phosphate $Al_2(PO_4)_2$ obtained by precipitation and well washed, cannot be dyed with alizarin. The formation of a lake only occurs when a calcium salt, *e.g.* calcium acetate, is also added. Aluminium-calcium-alizarin lakes of varied composition may be prepared by boiling together definite proportions of pure aluminium hydroxide, calcium acetate solution, and alizarin. They form either dark or bright brownish-red precipitates. All are insoluble in water, and some are insoluble in ammonia. The amount of calcium entering into the composition of the lakes produced in this manner depends upon the amount of alizarin employed and *vice versâ*.

The probable formula of normal alizarin-red lake is given as $Al_2Ca(C_{14}H_6O_4)_3(OH)_2$ by the above-mentioned authors.

Cochineal-carmine. In the preparation of this brilliant scarlet-lake, cochineal is extracted in tin-lined vessels with a large quantity of boiling water. Certain additions are made to the filtered decoction, and it is then allowed to stand for several weeks, or even months, in shallow vessels of tin or porcelain, during which period the carmine gradually separates in the form of a fine red powder. The additions referred to vary with different makers, and include the following: potassium binoxalate, acid potassium tartrate (cream of tartar), alum with or without cream of tartar, hydrochloric acid, &c. In all cases the presence of iron must be strictly avoided. The necessary ingredients may also be added to the water with which the cochineal is boiled, in which case the decoction must be filtered hot, since it rapidly becomes turbid on cooling. The addition of gypsum, calcium carbonate, zinc oxide, &c., so usual in other cases, must be avoided, since these would produce violet-coloured lakes.

The manufacture of cochineal-carmine is now very restricted, and the methods employed for producing the finest product have always been kept secret.

According to Alyon and Langlois 500 grams cochineal are boiled for 1½ hours in 30 litres water containing 25 grams sodium carbonate. The decanted solution is well stirred up with 25–35 grams powdered alum, and then allowed to settle about 20 minutes; the clear liquid is poured off, a dilute solution of isinglass or albumen is added, and the whole is heated until the carmine collects together in the form of a coagulum. After cooling and allowing to settle, the supernatant liquid is decanted off, the carmine is collected on a filter, washed, and dried at a low temperature. The deeply coloured filtrate serves for the production of carmine-lake.

Even alum alone could apparently be used as the precipitating agent, according to an old recipe, but it seems likely that in this case water possessing an alkaline reaction must of necessity have been employed. Boil 16 parts ground cochineal for 10 minutes with about 600 parts of water, then add 1 part ground alum, boil a few minutes longer, filter the hot solution and allow the filtrate to stand in shallow porcelain basins. In the course of a few days the carmine is said to separate in the form of a red slimy precipitate, which is collected and dried. The decanted liquor on standing yields a further quantity of carmine of a lower quality; its precipitation is facilitated by the addition of a small quantity of stannous chloride.

The residual cochineal which has thus been only partially exhausted serves for the preparation of carmine-lake.

In other similar recipes a mixture of alum and cream of tartar is used instead of alum only, but in that of Madame Cenette, at one time a celebrated maker of carmine, the statement that the effective precipitating agents are potassium nitrate and potassium binoxalate is difficult to understand.

Chinese carmine is said to be prepared by extracting cochineal with a boiling solution of alum, heating the filtered decoction with the addition of a solution of tin in nitric and hydrochloric acid (*aqua regia*), and finally leaving the liquid to stand till the carmine separates.

Cochineal-carmine is insoluble in water but soluble in alcohol. In ammonia solution it dissolves readily with a purplish-crimson colour;

from this solution tartaric acid precipitates the original carmine, for although when dried the precipitate has a brownish-red colour it becomes bright red when powdered. The following analysis of cochineal-carmine is given by C. Liebermann (Ber. 18, 1969):

Moisture	17 p.c.
Nitrogenous matter	20 ,,
Ash	7 ,,
Colouring matter	56 ,,
Wax	traces

The ash consists of SnO_2 0·67 p c., Al_2O_3 43·09, CaO 44·85, MgO 1·02, Na_2O 3·23, K_2O 3·56, P_2O_5 3·20. From these analyses Liebermann considers cochineal-carmine to be a peculiar aluminium-calcium-protein compound of the carmine colouring matter, somewhat analogous to the Turkey-red lake, in which alizarin is combined with aluminium and calcium. According to the experiments of the late J. Bedford of Leeds, cochineal-carmine can only be prepared if a calcareous water is employed, or if calcium salts are added during the reaction. Cochineal-carmine can, indeed, be readily produced by adding to a cold extract of the dye prepared with a hard water potassium carbonate, alum, and subsequently cream of tartar (or potassium binoxalate) in definite proportion. The carmine precipitate separates very gradually during some days, and has an extremely brilliant character. If a small quantity of stannic chloride is also added to the mixture the precipitation is hastened and the product possesses a more scarlet tint (private communication).

Carmine-lake is simply an ordinary aluminium or tin lake of the colouring matter of cochineal, produced by adding sodium carbonate to a cochineal decoction containing alum or stannous chloride, or both. The latter may also be added to an alkaline solution of the colouring matter.

Florentine-lake is merely a special quality of carmine-lake, containing usually an excess of alumina, and sold in the form of ‘drops’; and the so-called Venetian-lake, Hamburg-, Chinese-, Roman-, and scarlet-lakes, are all varieties of Florentine-lake.

Brazil Indian-lake or lac-lake is a dark purplish-red lake analogous to carmine-lake, and prepared in a similar manner from the Indian product ‘lac.’

Brazilwood-lake can be prepared by extracting Brazilwood or peachwood with boiling water, adding alum and tin solution to the filtered decoction, and finally precipitating with sodium carbonate, avoiding excess. Another method is to add precipitated and washed aluminium hydroxide to a filtered decoction of Brazilwood. Freshly prepared decoctions are never suitable for the manufacture of these lakes as they should always be oxidised, by exposure to air or otherwise, in order to change the principle brazilin into the necessary colouring matter brazileïn.

Vienna-lake is a species of Brazilwood-lake, prepared in the following manner: A mixture of ground starch (30 kilos.), chalk (10 kilos.), and a little gypsum, is stirred up with a decoction of Brazilwood; then ground alum (1 kilo.) is added and the whole is well stirred for 12 hours and finally allowed to settle. After decanting the clear liquor, Brazilwood decoction is again added to the residual precipitate, together with a further quantity of alum (1 kilo.), and the stirring is continued as before. This process is repeated until the precipitate has taken up sufficient colouring matter and acquired the character of a lake. The decanted liquors are agitated with fresh starch, chalk, &c., in order to yield further quantities of lake.

In the foregoing process the alum is decomposed by the chalk, and the alumina precipitate thus produced combines with the colouring matter. At first the lakes appear violet through the presence of excess of chalk, but with the continued addition of alum they gradually acquire a crimson colour.

Fine dark carmine-red lakes are obtained by adding stannous chloride and cream-of-tartar to a concentrated old decoction of Brazilwood.

Yellows.

Persian-berry lake is prepared by extracting Persian-berries two or three times with boiling water, dissolving alum in the combined and filtered liquors, and then precipitating with sodium carbonate, taking care to avoid excess. The precipitate is collected on a filter, washed, and sold in the form of paste. This lake, containing much starch, and sold in the dry form, is said to be employed in the colouring of sweetmeats.

Persian-berry carmine is produced if stannous chloride is employed instead of alum in the above process. It is a bright orange lake employed by calico-printers.

Persian-berry lakes may also be made after the manner of Vienna-lake, *i.e.* with the use of chalk, alum, and starch.

It is essential to employ only freshly prepared decoctions if bright-coloured lakes are desired.

The following procedure is described by Zubelon (Bull. Soc. Ind. Mulhouse, 1919, 84, 5[illegible]1): The berries are extracted to form an infusion of 2°–3°Bé. (sp.gr. 1·013–1·020). Solutions of salts of tin and aluminium are then added, and the liquor is neutralised with 300 litres of caustic soda solution. The ingredients required are: 300 kilos. Persian berries, 90 kilos. of tin salt, 15 kilos. of potash alum, and 31 kilos. of caustic soda. If the neutralisation be performed at 50° immediately after the addition of the mordants, no rhamnetin is produced, and the canary-yellow lake corresponds to xanthorhamnin. By operating at 100° some rhamnetin is formed and the lake has an orange shade. By working between 50° and 100° and allowing the acid salts to react for a quarter of an hour before neutralising, shades ranging from canary-yellow at 50° to deep orange at 100° may be obtained, according to the proportion of rhamnetin produced (J. Soc. Chem. Ind. 1919, 712, A.).

Quercitron-yellow lake, Flavin-lake, or Dutch-pink is made according to the method adopted in the case of Venetian-lake, by precipitating a decoction of quercitron-bark containing alum with chalk. The methods employed in making yellow lakes from Persian-berries may also be used. To ensure bright colours the decoction of quercitron bark is clarified by adding a little gelatin solution, thereby removing the tannic acid. Sometimes milk of lime is used instead, taking care to avoid excess.

It is said that these quercitron colours retain their intensity by gaslight better than all other vegetable yellows, and are hence useful for theatre decorations, &c.

The yellow natural colouring matters, especially flavine and Persian berries, are still in some demand for the production of green lakes by combination with basic green artificial colouring matters.

The yellow-lake is first prepared and a solution of the coal-tar colour precipitated upon it by tannin and tartar emetic. A partial precipitation of the basic colour is effected by the tannic acid in the vegetable colour, but must be completed by a further addition. These lakes are used for wall papers and for colouring toys.

Stil de grain is a low quality of Dutch-pink.

English- and **Italian-pinks** are other qualities of quercitron-bark yellow lakes.

The above lakes are sold in the dry condition in the form of pyramidal-shaped 'drops.' They never possess the brilliancy of those obtained from Persian-berries.

Lakes from vegetable colouring matters have no longer their former importance, and there can be little doubt that most of them will eventually become obsolete.

Lakes derived from Artificial Colouring Matters.

The great increase in the number and variety of coal-tar colouring matters has given rise to a corresponding increase in the colour lakes made from them. Moreover, many of the lakes so formed are at least as fast as any obtainable from natural colouring matters. In consequence the latter have lost much of their former importance.

In the preparation of these lakes the 'base' or 'carrier' upon which the colouring matter is precipitated in a more or less insoluble form is a most important element, since it determines in great measure their brilliancy, covering power, and general qualities.

On the other hand, upon the character of the colouring principle depend other properties of the lake, *e.g.* fastness to light, to spirit, to alkalis and acids.

'Carriers' for lakes are usually very finely divided, insoluble, white (more rarely coloured) materials, such as starch, kaolin (China clay), gypsum, heavy spar (barytes), artificial barytes (blanc-fixe), lithopone, precipitated chalk, kieselguhr, zinc white, red lead, &c. They are intimately mixed with the colour solution, and attract the colouring matter either directly or when suitable precipitating agents are added to the mixture. More often, however, they are formed and precipitated along with the colouring matter, and may then consist of aluminium hydroxide, phosphate, or arsenate, or the first named along with barium sulphate.

The precipitating agent to be employed in any particular case varies according to the nature of the colouring matter—whether acid or basic, for example—and the purpose for which the lake is intended. For lakes employed in decorative painting finely ground barytes is considered to be the most serviceable 'carrier.' Gypsum and kaolin are also used. The chief base for lakes employed in printing wall-papers is blanc-fixe, since it excels all others in giving body and covering power; usually some quantity of alumina, starch, or China clay is admixed with it to render the resulting lake lighter and easier to work. Higher-class papers contain a proportionately greater amount of alumina. For paper-staining, lithographic, and printing inks the lakes must possess fineness and covering power to a very high degree, and for these aluminium hydroxide, precipitated apart from the colouring matter, is highly esteemed. It is particularly valuable in producing lakes of a transparent nature for use in the three-colour process; some blanc-fixe is often precipitated together with the alumina. Starch, China clay, zinc white, and lithopone are also employed where transparency in the pigment is not of primary importance.

China clay is most largely used with the basic coal tar colours, since for these its attractive power is very marked. Barium sulphate and aluminium hydroxide precipitated during the process of forming the lake, are chiefly used with the azo colours and the acid colouring matters generally. Lead sulphate and red lead are important bases for the eosin lakes.

The proportions of the various materials employed in making the lakes vary considerably according to the desired intensity of the final product.

All lakes should be washed with water, preferably by decantation, till neutral and free from soluble salts. They are sold as pastes or powders, the latter being sometimes in the form of light porous blocks or 'drops' of suitable size.

In all cases the 'extra' brands of all colouring matters should be purchased. They contain the dyestuff in a more highly concentrated form, for ordinary brands are standardised for the use of the dyer by the addition of starch, common salt, or sodium sulphate, and these are useless, or even harmful, from the point of view of the lake manufacturer.

A. *From Basic Colouring Matters.*

The chief methods of precipitating basic colouring matters are—

(*a*) With tannic acid; (*b*) with soap or sulphonated oil; (*c*) with sodium phosphate or arsenate; (*d*) with resin soap; (*e*) with casein or albumen.

(*a*) Tannic acid is the most generally used of all precipitating agents for basic colouring matters, combining with them to form tannates insoluble in water. It is but rarely used alone, since the resulting lakes are dull and extremely fugitive; an addition of half the equivalent quantity of tartar emetic causes the complete fixation of the lake, and improves its properties as regards brightness, fastness to light, spirit, &c. Sodium acetate, or occasionally sodium carbonate, is employed to reduce the acidity of the solution.

The 'carrier' is well mixed with water, the solution of the colour added together with sufficient sodium acetate to combine with the mineral acid liberated by the colour base. The solution of tannic acid is next poured in whilst stirring well, and the precipitation completed with tartar emetic.

This method is most suitable for green and red colours, such as malachite green, brilliant green, magenta, rhodamine, and safranine.

(*b*) A method especially suitable for violet and blue basic colours is based on the precipitation of their colour bases as salts of oleic, palmitic, and stearic acids. A pure soap, containing no free alkali, or a sulphonated olive oil (*e.g.* Turkey-red oil) is employed. Aluminium sulphate, tannic acid, zinc or tin salts are also added on occasion.

(*c*) For basic colours of the methyl violet class a further method consists in the precipitation of aluminium phosphate, together with the added colour by means of aluminium sulphate and sodium phosphate to which sufficient sodium carbonate has been added to produce a perfectly neutral solution.

$$Al_2(SO_4)_3+2Na_2HPO_4+Na_2CO_3 \\ =Al_2(PO_4)_2+3Na_2(SO_4)+H_2O+CO_2$$

Similarly sodium arsenate, freshly prepared from white arsenic and sodium carbonate, is used in place of sodium phosphate—no addition of soda is then necessary, but care must be taken that the solution is neither strongly acid nor alkaline. As a rule, the precipitation is made in a very slightly acid solution obtained by using a slight excess of aluminium sulphate with addition of sodium acetate.

(*d*) All basic colouring matters form lakes of great brilliancy with resin soap, *i.e.* a solution of colophony in caustic or carbonated alkali. They are precipitated on the carrier along with a metallic salt of the resinate, usually zinc or aluminium.

Auramine, magenta, rhodamine, and patent blue furnish the most satisfactory lakes, and are much used for wall papers. They are of no value for oil or lithographic work, being very fugitive and readily soluble in alcohol and benzene.

It has been found possible to use the benzene solution of these 'resinate' colours for dyeing silk without injuring its finish, lustre, and general appearance. They are also used for preparing coloured varnishes employed in ornamenting metallic surfaces, wood, leather, glass, &c.

(*e*) According to Weber albumen can be employed as a precipitating agent for basic colouring matters with production of lakes of excellent brilliancy, notably fast to water and light. A cold aqueous solution of the dyestuff is mixed with the albumen (also in aqueous solution), stirred into the carrier, and the whole precipitated by raising the temperature to 90° with or without the final addition of a little acetic acid.

Casein may also be applied in a somewhat similar manner.

It is stated that this method is also applicable to the acid colouring matters, and is of special importance for producing non-poisonous eosin and rhodamine lakes.

Blue and violet lakes of great brilliancy may be obtained by mixing certain blue and red colour solutions with precipitated and washed Prussian-blue, which thus becomes dyed.

Potassium dichromate along with starch, &c., has been used as a precipitant with safranine, with which it produces a brownish-red lake changing to carmine-red on drying.

Basic colouring matters are especially remarkable for their ready absorption by inert materials, such as kaolin, starch, diatomaceous earth, green earth, &c., without the aid of any precipitating agent. A solution of the dyestuff is well mixed with the finely divided and well-washed base, and allowed to stand for some time with occasional stirring. A certain amount of colouring matter is attracted from the solution and the carrier becomes, as it were, dyed. Other carriers, *e.g.* gypsum, blanc-fixe, zinc oxide, &c., may be used, but their attractive power for the colouring matter is very small, and they serve chiefly as diluents. The lakes from the silicious earths are the more firmly fixed, and withstand the action even of strong alkalis. For this reason they find application in the manufacture of cheap lime washes.

Coloured powders, prepared according to these latter methods, can scarcely be regarded as true lakes, as they mostly give up their colouring matter on repeated washing.

B. *From Acid Colouring Matters.*

The great majority of the acid colouring matters referred to here are the sulphonic acid derivatives of certain colour bases and azo colouring matters derived from benzene, naphthalene, &c. With these barium chloride is almost exclusively employed as the precipitating agent; a further addition of aluminium sulphate is also often made, especially if the colouring matter exhibits mordant dyeing properties according to the law of Liebermann and v. Kostanecki.

More rarely, lead salts replace barium chloride.

Some of the phenolic colouring matters which possess special features may be included under this head, notably the eosins. Lead acetate or nitrate is especially suitable as a precipitating agent for colours of this class.

Other suitable materials are alum, aluminium acetate, calcium, magnesium, zinc, or stannic salts; as a rule, they are used in conjunction with caustic or carbonated alkali.

As in the case of the basic colour lakes, so here, the 'base' or 'carrier' upon which the lakes are precipitated is of great importance, and the reader is referred to what has been said already upon this point.

The standard method for the formation of lakes from acid colouring matters containing the sulphonic acid group is that with aluminium sulphate and barium chloride. The aluminium sulphate is precipitated as hydroxide in the first instance by soda, the colouring matter stirred in and then precipitated by the addition of barium chloride. In this way part of the 'carrier' is also produced, in the form of artificial barytes, at the moment of precipitation through the interaction of the barium chloride and the sodium sulphate resulting from the decomposition of the aluminium sulphate, and not only is the precipitation rendered more complete thereby, but also a very intimate admixture of the 'carrier' and precipitated colour is secured.

A proportion of inert 'carrier,' *e.g.* heavy spar, kaolin, lithopone, may also be added to the solution of aluminium sulphate before precipitation when lakes of greater opacity or less tinctorial power are desired; an extra addition of Glauber's salt before the final precipitation, will bring about the same result by increasing the amount of artificial barytes produced. Replacing the aluminium sulphate by alum yields lakes of a higher quality and valuable for printing purposes. They are, of course, more costly to manufacture.

A typical example of this method, published by the Farbwerke vormals Meister Lucius and Brüning, Hoechst am Main, is the following:—

30	parts	aluminium sulphate	1/100	solution
12	,,	calcined soda .	1/100	,,
12	,,	colouring matter .	1/50	,,
42	,,	barium chloride .	1/100	,,

Precipitate at 50°-60°C. This method is stated to be suitable for the various brands of azo scarlets.

Reds. These are chiefly derived from the azo colouring matters. A great variety are now on the market, furnishing shades from a very bright scarlet to a dark bluish-red. Such are Ponceau 2G, G, GR, R, 2R, 3R, &c., Fast red, Bordeaux red, Crocein scarlet, &c.

Red lakes, in nearly all cases, are shaded by admixture with other colours, especially the various brands of oranges (*see* below under *Combined Lakes*). In such cases it is of considerable importance whether the colours are dissolved separately or together, the latter method often producing brighter lakes than the former.

Generally speaking, complete precipitation is obtained by the use of barium chloride upon a 'base' of alumina with or without the admixture of an inert diluent, blanc-fixe being produced simultaneously with the precipitation; certain colours are more difficult to throw down completely, but this may be obviated by suitable variations of quantities, temperature, dilution, &c. The addition of a little Turkey-red oil frequently has a favourable influence.

Another method in the case of some red azo colouring matters consists in treating a solution of aluminium sulphate with milk of lime, forming a 'base' of alumina and calcium sulphate. The colour is thrown down upon this by the addition of barium chloride, and at the same time the calcium sulphate is replaced more or less completely by blanc-fixe. The resulting lakes are said to be very soft and light.

The milk of lime may be replaced by levigated chalk with advantage.

Eosins. These colouring matters give scarlet and crimson lakes of great brilliancy, some of which (the so-called 'vermilionettes') are employed as substitutes for vermilion. They are mostly very fugitive. For yellowish-reds a yellow shade of eosin is employed; for reds, gradually increasing in blueness, erythrosine, phloxine, cyanosine, and rose bengal may be used. The usual precipitants are lead salts, 1 part pure eosin being precipitated by 1 part lead acetate, or 0·75 lead nitrate. Aluminium, tin, and zinc salts are also used.

The nature of the precipitating agent influences the shade of the resulting lake; thus lead acetate gives more yellowish products than lead nitrate from the same colouring matter. Lead salts give blue, tin and aluminium salts yellow shades.

For 'vermilionettes' red lead is a suitable base, with or without the addition of small quantities of lead sulphate or barytes. Better class varieties are made with chromate-of-lead-orange and alumina, in order to lessen their high specific gravity. Due allowance must be made for the variation in shade caused by the presence of a coloured 'carrier.' Their production is very simple; the solution of colouring matter is mixed with the base, complete precipitation being obtained on the addition of a lead salt.

Printing and lithographic colours (known as *geranium*-lakes) are largely produced from the eosin colouring matters. They may be transparent or opaque, according to the special use for which they are intended; they all possess great covering power. Alumina and blanc-fixe—either alone or in conjunction—and lead sulphate are chiefly used as the 'carriers'; or, occasionally, starch, kaolin, or red lead. The colour is precipitated upon them by a lead salt. Aluminium (as alum, &c.) does not produce so complete a precipitation.

If desired the lake may be shaded up by the addition of rhodamine B, which unites with, and is precipitated along with the eosin.

Combined lake pigments are also made with the various brands of azo scarlets and orange II.

Oranges. The methods applicable to the red colouring matters are also suitable for making orange lakes.

Orange II. furnishes a bright lake of good fastness to light, and is in considerable demand on account of its cheapness. Other brands are orange R, O, and fast orange O. For better-class lakes used in printing and lithography brilliant orange G and R are employed.

As stated above, orange colouring matters find frequent application in shading the scarlet azo colours.

Yellows. The number of yellow lakes is comparatively small owing to the superior properties of the various chrome yellows (*see* PIGMENTS). They are employed, however, to shade green lakes in a manner similar to that of the oranges for azo scarlets.

The most important colours used are naphthol yellow S, quinoline yellow S, Victoria yellow, &c.

Greens. The colouring matters mostly employed for these lakes are sulphonic acids of the triphenylmethane series, *e.g.* the various acid greens, but are among the most difficult of all the acid colouring matters to precipitate.

Naphthol green belongs to a different class.

They are only partially precipitated by barium chloride, employing the usual aluminium sulphate and soda method, and special modifications must be resorted to, such as after-precipitation with further quantities of aluminium sulphate or barium chloride, or both at once, reversing the order of precipitation and so on.

The lakes from acid greens (the so-called viridine greens) possess a bluish-green shade. Lakes from naphthol green are particularly fast to light. Better results and a greater range of shades are obtained by admixture with naphthol yellow or quinoline yellow. Combination apparently takes place with the basic amino groups of the acid green with the formation of a less soluble combined colour.

Blues. With the exception of the red acid colouring matters the blues furnish the greatest number of colours for lake-making. A large number of shades are obtainable, but, unlike the scarlets, a separate brand is used for each particular shade, and mixtures are rarely found necessary. Alkali blues (opal blue, water blue, &c.), patent blue, and erioglaucine are chiefly in demand. They are readily precipitated by barium chloride upon a mixed alumina and blanc-fixe or other suitable base. The patent blues and erioglaucines are exceptions; for the former the addition of a little barium hydroxide has been found effective, for the latter some zinc sulphate is added, and this is precipitated by sodium carbonate as mixed hydroxide and carbonate.

For printing purposes alkali blue can be precipitated by Turkey-red oil or soap, and subsequent addition of a lead or aluminium salt, with a suitable carrier. The latter, again, may be dispensed with, and in such cases the lakes often exhibit a magnificent lustre.

Violets. Very few violet lakes are manufactured from acid violet dyestuffs, although they are very much faster than the corresponding lakes from basic colours. Fast acid violet is principally employed. They are all expensive to make, and only find application for special purposes.

A very blue violet is formyl violet S4B; it furnishes lakes suitable for the manufacture of printing inks.

All these colours are precipitated by barium chloride upon a suitable 'carrier.'

C. *From Mordant Colouring Matters.*

Besides the very important alizarin-red lakes already described, a certain number of other adjective colouring matters are used for lake making. They are mostly closely related to alizarin itself, *e.g.* alizarin orange, brown, bordeaux, yellow, green, black, blue; acid alizarin blue, and galloflavin, cœrulein, and gallein are also employed. They furnish lakes very fast to light, although they cannot compare in brilliancy of shade with other, but much more fugitive lakes from basic and acid colours.

Lake formation is brought about in the same manner as with alizarin red, the general principle involved being the precipitation of an alkaline solution of the colour by aluminium hydroxide.

Colours which do not dissolve in soda require a modification or reversal of the usual method; they are stirred up with the solution of aluminium sulphate (or alum), and combination is effected by addition of soda, sodium phosphate, and Turkey-red oil.

The Badische Anilin und Soda Fabrik publish a special method for cœrulein:

22 lbs. colouring matter in 27½ gallons of water with 44 lbs. sodium bisulphite (40°Bé.) are well mixed and allowed to stand for 12 hours; then heated to 70°C. with a further 27½ gallons of water, filtered, and the filtrate diluted with 110 gallons water. The whole is then raised to boiling, and 44 lbs. potassium alum added. After half an hour's boiling a final addition of 33 lbs. sodium bisulphite is made, the boiling again continued for half an hour, and the lake filtered, washed, and dried at the ordinary temperature.

D. *From Insoluble Colouring Matters.*

A series of azo colours insoluble in water are now made by the principal colour-works and sold in paste form for working up into lakes, according to specially adapted methods. The range of shades varies from yellow to bluish-red.

They are mixed with suitable 'carriers' such as heavy spar, lithopone, orange lead, magnesium oxide, and chalk. Frequently the mixture is simply ground together in the cold; another method is to heat to boiling and add barium chloride. Salts of magnesium, copper sulphate, and ferrous sulphate with Turkey-red oil are also used. The dry lakes are subjected to prolonged grinding with zinc white, orange lead, &c., this process greatly increasing their intensity. They are employed for lithographic and printing inks, as well as for oil and varnish colours and possess good brilliancy; many of them are exceptionally fast to light as well as to alkalis and spirit.

E. *From Developed Azo Colours.*

The application of the 'ice colours' to carriers for the production of lake pigments was a natural outcome of their successful use upon textile fibres.

At the present time the method is in very general use as the lakes made after this manner are distinguished by their fastness to light and other valuable properties. Practically all shades are obtainable except a green.

The pigments are all produced by the diazotisation of an amine followed by coupling with a phenol or another amine in a solution which contains the 'base' or 'carrier' in suspension.

The chief amines used in diazotising are: *m*- and *p*-nitraniline, the nitro-toluidines, anisidine, nitrophenetidine, benzidine, tolidine, α- and β-naphthylamines. Bluer shades, but less fast to light, are obtained from aminoazobenzene and -toluene.

The diazo compounds are coupled with various phenols and amines, especially β-naphthol which produces very bright lakes fast to water (the *insoluble azo-colours*). Other phenols used are phenol itself, resorcinol, α-naphthol, and its disulphonic acid, and β-naphtholdisulphonic acid.

The principal amines are diphenylamine and *m*-phenylenediamine.

Certain precautions are necessary to produce lakes of maximum brightness, *e.g.* care must be taken to regulate the proportions of acid and alkali so that a neutral liquor is present when the formation of the lake is complete. In practice a little sodium acetate is added, acetic acid having a less harmful action than free hydrochloric acid. An alkaline liquor renders the lake dull and dirty in shade.

The following recipes (published by Chem.

Fabrik (Griesheim-Elektron) will best illustrate the manufacture of these lakes:

A base (A) is prepared from solutions of
1330 grams aluminium sulphate,
650 ,, calcined soda,
490 ,, barium chloride.

The precipitate is washed thoroughly and well mixed with the alkaline solution of β-naphthol (B) prepared from
300 grams β-naphthol dissolved in
300 c.c. caustic lye (34°Bé.) and 2 litres boiling water.

Add 300 grams calcined soda in 3 litres cold water,
180 grams Turkey-red oil,
300 grams sodium acetate, making the whole up to 10 litres.

Into this is run the diazo solution (C) from
180 grams p-nitraniline dissolved in
600 c.c. hydrochloric acid (21°Bé.) and 2 litres boiling water.

The temperature of this liquid is then reduced to 10°C. by addition of 2 litres cold water and ice and then diazotised with a solution of 144 grams of sodium nitrite.

The precipitated lake is washed thoroughly and dried. The above recipe is said to yield a deep-red shade.

The azophor reds of M.L.B. may be used in place of the diazotised bases.

F. *From Sulphide Colouring Matters and Indigo.*

Within recent years a number of processes have been patented for the manufacture of lake pigments from the vat dyestuffs, especially the sulphide colours. They are brought into solution as in dyeing cloth and precipitated upon a base by various means.

According to one such patent, taken out by Cassella & Co., the dyestuff (25 p.c. paste) is dissolved in 1 p.c. sodium sulphide and precipitated upon barytes or other suitable 'carrier' by the addition of sodium carbonate and barium chloride.

In another method, patented by the Berlin Aniline Co., the dyestuff is dissolved in sodium sulphide, a solution of barium chloride added, and oxidation brought about by blowing air through or adding manganese dioxide.

For instance, 20 parts sulphur black T extra are dissolved in a solution of 15 parts sodium sulphide, a solution of 25 parts barium chloride run in and air blown through the mixture.

Lakes may also be obtained from indigo. They are said to be exceptionally fast and especially suitable for producing very bright combined lakes.

Combined Lake Pigments.

As already mentioned a lake is frequently produced by the precipitation of more than one colouring matter, either separately or in conjunction, upon the 'carrier.' The colours may be of similar chemical nature, but varying shade, or they may differ absolutely in both these respects. To the first class belong, for example, the numerous scarlet lakes obtained by combining orange and scarlet colouring matters of various shades.

Lakes belonging to the second class differ materially both in shade and properties from any member of the combination used to produce the pigment, *e.g.* the maroon lakes made from scarlets combined with magenta or safranine.

For the latter lakes and others of the same class the initial colour is always either red, orange, or yellow, and from these all possible shades from bluish-red to yellowish-green are obtained by the addition of other colours such as magenta, safranine, methylene blue, malachite green, acid green, and even diamond black.

The methods available for manufacturing these combined lakes are obviously too numerous for detailing here, but a few general outlines and precautions may be indicated. Thus due consideration must always be given to the acid or basic character of the colours used and suitable means of precipitation arranged. Acid and basic colours should never be dissolved together, since combination takes place often with the production of a dark resinous precipitate. The same applies to colours such as the acid greens, which contain groups capable of combining with the acid or basic groups of the second colour.

The first colour may be made into a pigment (termed the 'initial lake'), upon which a second colour is then precipitated by suitable reagents. When, as most frequently happens, the initial lake is prepared from a soluble azo colour by means of barium chloride, and a basic colour is thrown down upon it, care must be taken that the precipitating agent used in the latter case does not affect the pigment first formed. For this reason materials such as Turkey-red oil and resin soap must be excluded, and the tannic acid and tartar emetic method is the only one really suitable for this purpose.

Analysis of Lake Pigments.

The analysis of the colouring matters in a lake is often a matter of great difficulty, and the subject remains largely in an empirical state. The composition of the 'base' or 'carrier,' on the other hand, presents no serious difficulties; a portion of the lake is incinerated and the residue examined by the usual processes of qualitative analysis. In this way the presence of mineral pigments to which coal-tar colours have been added may also be detected. Valuable indications may often be given by the presence of the precipitating agent in the mineral residue, *e.g.* a red lake which is found to contain lead is most likely to have been produced from a colouring matter of the eosin series, &c.

Other properties, chemical and physical, also furnish important evidence, the colour, fastness to light, to acids, alkalis, spirit, &c. Further, the selling price of a lake will often be a deciding factor where two colours are under consideration, of similar shade but different in price.

The class of colouring matter from which any given sample of a lake may have been derived can generally be settled with considerable precision by employing the schemes drawn up by various authors for the analysis of dyestuffs, both on the fibre and in the solid state, making allowance for the alterations in properties brought about by the presence of the carrier and precipitating agent. The identification may be carried further by noting the behaviour of the sample towards such reagents as sulphuric acid, caustic soda, hydrochloric acid, alcohol, &c.; but where more than one colouring matter is present the only satisfactory method of determining the shading colours is by trials in the laboratory or by comparison with a series of standards. Modern pigments, as previously stated, are mostly examples of 'combined' lakes, and in such cases, though the principal constituent may be identified, it is frequently all but impossible to detect the small quantity of the secondary colours present by any process of direct analysis. In this case it is best to ascertain their nature indirectly by a comparison with lakes specially prepared for the purpose.

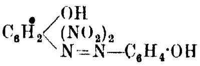
Literature.—Lehrbuch der Farbenfabrikation, J. G. Gentele; Die Erd-Mineral-und-Lack-Farben, &c., S. Mierzinski; Die Chemie des Steinkohlentheers (2nd ed.), 2, 22, G. Schultz; The Manufacture of Lake Pigments from Artificial Colours, F. H. Jennison; A Treatise on Colour Manufacture, Zerr and Rübencamp, translated by Ch. Mayer; The Manufacture of Mineral and Lake Pigments, Bersch, translated by A. C. Wright; Painters' Colours, Oils, and Varnishes, G. H. Hurst; Journ. Soc. Dyers and Colourists (1890, 6, 32); Instructions issued by several Coal-tar Colour Manufacturers: Weber (J. Soc. Chem. Ind. 1891, 10, 896; 1893, 12, 650; 1894, 13, 1151).

For the analysis of lake pigments.—Tests for Coal-tar Colours in Aniline Lakes, Geo. Zerr, translated by Mayer. A. G. P.

LAMPBLACK is the soot or finely divided carbon produced by the imperfect combustion of various substances of a fatty or resinous nature, such as vegetable and animal oils, pinewood, and dead oil; and it may be taken that whatever the combustible material which, on full exposure to the oxygen of the air, produces the best illumination, that material will, if partially deprived of air, produce the greatest amount of sooty deposit. The German mode of manufacturing lampblack consists in collecting it on a woollen cloth exposed to the smoke emitted from resinous woods burning in a close furnace. The cloth being shaken from time to time, the particles are detached and collected. Lampblack is employed in the manufacture of printing-inks and pigments.

What is known in American trade as *carbon black* is a fluffy, velvety form of lampblack produced by the incomplete combustion of natural gas containing ethane, burning against a metal surface. It is made in various localities where supplies of natural gas are available, but mainly in West Virginia and Louisiana, which accounts for 90 per cent. of the total yield. One thousand cubic feet of gas yield from 1 lb. to 1¼ lb. of carbon black. Upwards of fifty-one million pounds were produced in 1920 from 39 plants. About 40 per cent. of the production is used as a colouring material in the rubber industry. 35 per cent. in manufacturing printer's ink, and 10 per cent. for various uses: *e.g.* stove and boot polish, gramophone records, black leather, electric insulators, drawing and marking inks, celluloid and carbon papers; about 15 per cent. is exported. Carbon black is used instead of zinc oxide as a filler for rubber tyres, as it increases their tensile strength and elasticity (U.S. Geol. Surv. 1921; Jour Soc. Chem. Ind., 1922, 60 R).

LANCASTER YELLOW



$$C_6H_2\begin{cases}OH\\(NO_2)_2\\N{=}N{-}C_6H_4{\cdot}OH\end{cases}$$

A colouring matter obtained by P. Greiss, in 1875, by the action of picramic (*iso*purpuric) acid on phenol. Sparingly soluble in water; soluble in sulphuric acid, with reddish-yellow colour. Dyes silk and wool in an acid bath brownish-yellow. No longer used.

LANGBEINITE. A double salt

$$K_2SO_4{\cdot}2MgSO_4$$

crystallised in the cubic system with tetartohedral symmetry,[1] and containing K_2O 22·7 p.c. Crystals are very rare, the mineral usually occurring in a granular massive form. This is colourless to grey with a glassy to greasy lustre and a conchoidal fracture; H. 3–4; sp.gr. 2·81–2·86; refractive index (Na) 1·5347. It is completely, though slowly, soluble in water. On exposure to the air it absorbs moisture, becoming cloudy, and finally falling to powder with a considerable increase in volume; the material then consists of a mixture of picromerite ($K_2SO_4{\cdot}MgSO_4.6H_2O$) and epsomite ($MgSO_4,7H_2O$). The mineral is found in considerable quantities at several localities in the Prussian salt deposits, where it was first recognised in 1891. At Wilhelmshall north of Halberstadt and near Wolfenbüttel in Brunswick it occurs as a primary mineral in the older beds of rock-salt, taking the place of polyhalite in places where calcium is deficient. At Westeregeln and Neu-Stassfurt it is found in association with sylvite and rock-salt, and is partly of secondary formation; and at Solvayhall near Bernburg it overlies the carnallite stratum. It is found also at Hall in Tyrol and in the Mayo salt mines in Punjab, India. At the last-named locality it was found with rock-salt, sylvite, and kieserite, and partly described in 1873 (F. R. Mallet, Min. Mag. 1899, 12, 159). The salt is prepared artificially from a boiling concentrated solution of magnesium chloride and potassium sulphate with excess of magnesium sulphate; or by fusing together potassium and magnesium sulphates in the proper proportions.

L. J. S.

LANOLIN *v.* CHOLESTEROL.

LANORESIN *v.* RESINS.

LANTHANITE. Hydrated carbonate of lanthanum, didymium, and cerium

$$R_2(CO_3)_3,8H_2O$$

crystallised in the orthorhombic system. An analysis by G. Lindström (1910) of material from Bastnäs, Sweden, gave: $(La,Di)_2O_3$ 28·34, Ce_2O_3 25·52, Y_2O_3 0·79, CO_2 21·95, H_2O 23·40, insol. 0·13=100·13. Crystals have the form of thin plates or scales with very nearly square outlines, or sometimes they are of a thick-tabular habit resembling apophyllite. They have a perfect micaceous cleavage parallel to the basal plane, on which the lustre is pearly. The colour is usually a delicate pink. Sp.gr. 2·6–2·74; H. 2½–3. The mineral occurs sparingly as an alteration product of cerite (*q.v.*)

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[1] The degree of symmetry is the same as that of crystals of sodium chlorate, but the crystals of langbeinite are optically inactive.

in gneiss at Bastnäs in Sweden; with zinc-ores in limestone at Bethlehem in Lehigh Co., Pennsylvania; with iron-ore at Moriah in Essex Co., New York; and at Canton mine in Cherokee Co., Georgia. L. J. S.

LANTHANUM. Sym. La. At.wt. 138·91 (Baxter, Pani and Chapin). Crude lanthana was obtained from the cerite earths in 1839 by Mosander, who afterwards separated this material by fractional crystallisation of the sulphates into lanthana and 'didymia' (neo- and praseo-dymia).

Sources.—The minerals containing the cerite metals, *e.g.* cerite, orthite, monazite, and lanthanite (native lanthanum carbonate containing didymium).

Separation. If the material employed as the source of lanthanum contains considerable quantities of yttrium earths a preliminary separation of the two main groups may be effected with sodium sulphate.

Methods of Isolation depending on Differences in Basic Strength.

The separation of lanthana from 'didymia' is quickly effected, although with some loss of material, by adding magnesia to a boiling solution of the mixed salts until the liquid ceases to give the characteristic absorption bands of neodymium and praseodymium, the less basic oxides of these elements being precipitated, whilst the more basic lanthana remains dissolved (Muthmann and Rölig, Ber. 1898, 31, 1718; R. J. Meyer and Marckwald, *ibid.* 1900, 33, 3009). Fractional precipitation with ammonia or caustic soda is hardly to be recommended for experiments on a large scale, because of the difficulty of collecting and washing the hydroxides. Moreover, ammonium salts are decomposed by lanthana and 'didymia,' so that these bases are not effectively removed from solution by ammonia.

An interesting modification of the basic method consists in utilising the ignited mixed oxides of the rare earth metals to precipitate fractionally an equivalent proportion of these metals from the neutral solution of their nitrates. A solution of the neutral nitrates is divided into two parts, one portion precipitated with oxalic acid, the oxalates ignited, and the resulting oxides added to the remaining portion of the nitrates in 12 p.c. aqueous solution. A vigorous action occurs, the mixture is diluted, heated on the water-bath, and the clear liquid decanted from the precipitate. The fractionation is repeated on both the soluble and insoluble portions. By this process the lanthanum accumulates in the solutions, whilst the praseodymium and neodymium are concentrated in the precipitates (Hermann, J. pr. Chem. 1861, 82, 385; Auer von Welsbach, Monatsh. 1883, 4, 630; *ibid.* 1884, 5, 508; Schottländer, Ber. 1892, 25, 378).

Boiling the rare earth oxides with ammonium salts leads to a fractionation, since the more basic constituents displace ammonia and pass into solution (Drossbach, Ber. 1902, 35, 2826).

The fractional decomposition of the nitrates is another method depending on differences in basic strength (Bettendorff, Annalen, 1890, 256, 159; Urbain, Ann. Chim. Phys. 1900, [vii.] 19, 184).

The mixed nitrates of lanthanum, praseodymium, neodymium, and samarium melt at about 400°–500° to a clear liquid, in which are gradually formed small crystals of basic nitrate. The solution obtained by boiling the product of fusion with 10 parts of water deposits the basic salt. The fusion is then repeated on the normal nitrates, from both the insoluble and soluble portions. The lanthanum accumulates in the undecomposed nitrate, while praseodymium, neodymium, samarium, together with terbium and yttrium metals are found in the basic nitrate fractions.

Methods of Isolation by Crystallisation.

By a systematic fractional crystallisation of the double ammonium nitrates

$$R(NO_3)_3,2NH_4NO_3,4H_2O$$

in nitric acid solution, Auer von Welsbach succeeded in separating lanthanum from the other cerite metals, and also in dividing 'didymium' into its components, praseodymium, and neodymium. In this fractionation lanthanum accumulates in the least soluble portions, and is followed successively by praseodymium and neodymium, whilst the most soluble fractions contain samarium and the terbium and yttrium metals (Monatsh. 1885, 6, 477). In operating on large quantities of cerite earths it is more convenient to work in neutral solutions rather than in nitric acid, but in the absence of acid the number of fractions is considerably increased (Wien Sitzungsber. 1903, 11A, 112).

Other modifications of von Welsbach's method have been devised, having for their object the more rapid separation of praseodymium and neodymium (*cf.* Schéele, Ber. 1899, 32, 409; Dennis and Chamot, J. Amer. Chem. Soc. 1897, 19, 799; Demarçay, Compt. rend. 1900, 139, 1019, 1185; Drossbach, Ber. 1902, 38, 2826; Lacombe, Bull Soc. chim. 1904, [iii.] 31, 570)

By each of these processes lanthanum can be readily separated in a highly purified condition, because it yields the least soluble double nitrates. Last traces of praseodymium are removed by fractional crystallisation of the double carbonates $K_2R_2(CO_3)_4$, $12H_2O$, where R—La, Ce, Pr or Nd, the metals being arranged in ascending order of solubility (R. J. Meyer, Zeitsch. anorg. Chem. 1904, 41, 94).

The classical 'sulphate' method may also be employed in separating lanthanum from the other cerite metals (Holtzmann, J. pr. Chem. 1858, 75, 321).

According to Dennis and Lemon (J. Amer. Chem. Soc. 1915, 37, 131) in the fractional electrolysis of a neutral solution of the nitrates of neodymium, praseodymium, lanthanum, and samarium, the lanthanum collects in the last fractions, and can thus be separated from the other earths of the didymium group. Lanthanum can be satisfactorily separated from praseodymium by this method.

Metallic lanthanum, m.p. 810°, sp.gr. 6·1545–6·193, sp. heat 0·04637, is best prepared by the electrolysis of the fused chloride, a current of 50 amperes and 10–15 volts being required; it is the most active of the rare earth metals, tarnishing in dry air, and in presence of moisture becoming coated with white hydroxide .

(Muthmann, Kraft and Weiss, Annalen, 1903, 325, 261; 1904, 331, 1).

When heated in air lanthanum furnishes a mixture of oxide and nitride, and in hydrogen it yields the hydride. With aluminium, lanthanum forms the alloy $LaAl_4$, a crystalline white substance (sp.gr. 3·923), stable in air, and insoluble in nitric acid (*cf.* Muthmann and Beck, Annalen, 1904, 331, 46).

Lanthana (*Lanthanum oxide*) is a snow-white powder produced by heating the hydroxide or oxalate; its sp.gr. is 5·94, or 6·53 after raising to white heat. The amorphous oxide readily absorbs water or carbon dioxide, but the crystalline modification (sp.gr. 5·295) obtained in rhombic prisms by heating lanthanum carbonate in fused borax can no longer be directly hydrated.

The oxide has been reduced to the metal by magnesium but not by aluminium.

Lanthanum hydroxide $La(OH)_3$, a white amorphous precipitate produced by adding excess of ammonia or caustic alkali to the solution of a lanthanum salt, is the strongest base of the rare earth series; it turns red litmus blue, absorbs carbon dioxide from the atmosphere, and displaces ammonia from ammonium salts. In the presence of hydrogen peroxide, the hydroxide gives a hydrated lanthanum peroxide.

Lanthanum hydride LaH_3 or LaH_2 (Winkler, Ber. 1891, 24, 873; Muthmann and Kraft, Annalen, 1903, 325, 279), formed by direct union of its components at 240°, is a black substance more stable in air than the corresponding cerium compound.

Lanthanum carbide LaC_2, sp.gr. 5·02, is prepared by heating in a carbon tube, with an electric current of 350 amperes and 500 volts, 100 parts of lanthana and 80 parts of sugar carbon. When decomposed with water the carbon yields 70–71 p.c. of acetylene, 27–28 p.c. of methane, and 2·0 p.c. of ethylene (Moissan, Compt. rend. 1896, 123, 148).

Lanthanum nitride LaN, a black powder prepared from lanthanum and nitrogen at red heat, is decomposed by moisture yielding ammonia and lanthanum hydroxide (Annalen, 1903, 325, 261). A basic lanthanum azide $La(N_3)_2{\cdot}OH,1\frac{1}{2}H_2O$ having explosive properties, is obtained by dissolving lanthana in aqueous hydrazoic acid, and precipitating with ether alcohol (J. pr. Chem. 1900, [ii.] 61, 408).

Lanthanum sulphide La_2S_3. A yellow powder, sp.gr. 4·9108, obtained by heating the anhydrous sulphate in hydrogen sulphide, is stable in air but decomposed by boiling water. A higher sulphide La_2S_4 has been produced by the further action of hydrogen sulphide on the sesquisulphide at 600° (Biltz, Ber. 1908, 41, 3341).

Lanthanum nitrate $La(NO_3)_3,6H_2O$ crystallises from water in transparent colourless prisms; it loses $5H_2O$ over strong sulphuric acid, and is readily soluble in alcohol. A strong solution of the commercial nitrate is used as a stamping fluid for marking the maker's name or brand on incandescent mantles, so that when these are burnt the design appears in brown on the white thoria skeleton.

Lanthanum ammonium nitrate

$$La(NO_3)_3,2NH_4NO_3,4H_2O$$

monoclinic crystals, is isomorphous with the corresponding double salts of the other cerite metals (Kraus, Zeitsch. Krist. 1901, 34 307).

Lanthanum magnesium nitrate

$$2La(NO_3)_3,3Mg(NO_3)_2,24H_2O$$

separates in lustrous colourless rhombohedral prisms belonging to the hexagonal system. Lanthanum also forms well-defined double nitrates with pyridine, quinoline, and other organic bases.

Lanthanum sulphate $La_2(SO_4)_3,9H_2O$ is the most stable of three hydrates, and the least soluble sulphate of the rare earth series, its solubility diminishing with rise of temperature; it separates in hexagonal prisms, isomorphous with the cerous salt $Ce_2(SO_4)_3,9H_2O$. The anhydrous sulphate is produced by heating the hydrate with strong sulphuric acid, when the acid sulphate $La(SO_4H)_3$ first produced is afterwards decomposed above 280°. The double sulphates $La_2(SO_4)_3,3K_2SO_4$ and

$$La_2(SO_4)_3,Na_2SO_4,2H_2O$$

are sparingly soluble, particularly in the presence of excess of alkali sulphate.

Lanthanum fluoride LaF_3 prepared in the anhydrous state by burning lanthanum carbide in fluorine (*cf.* Moissan, *l.c.*) and as a gelatinous precipitate $2LaF_3,H_2O$ by the interaction of hydrofluoric acid and lanthanum acetate; the sulphate yields the acid fluoride $2LaF_3,3HF$.

Lanthanum chloride $LaCl_3$, m.p. 907°, sp.gr. 3·947, is prepared by the general methods for preparing anhydrous chlorides (*cf.* Cerium; and Matignon and Bourrion, Compt. rend. 1904, 138, 627; 1905, 140, 1181; Ann. Chim. Phys. [viii.] 5, 127); it is a colourless compound dissolving in water or alcohol with considerable generation of heat. In aqueous solution this salt shows very little hydrolytic dissociation; its hydrate $2LaCl_3,15H_2O$ or $LaCl_3,7H_2O$ forms triclinic crystals, the alcoholate is $LaCl_3,2C_2H_5.OH$ (Zschiesche, J. pr. Chem. 1868, 104, 174; Cleve, Bull. Soc. chim. 1874, [ii.] 21, 196). The following double chlorides $2LaCl, 3PtCl_4,24H_2O$; $LaCl_3,PtCl_4,13H_2O$; and $LaCl_3,AuCl_3,10H_2O$ have been described.

Lanthanum platinocyanide

$$2La(CN)_3,3Pt(CN)_2,18H_2O$$

forms yellow fluorescent prisms with a blue reflex.

Lanthanum-cobalticyanide

$$La_2(COC_6N_6)_2,9H_2O$$

one of the most soluble of the rare earth cobalticyanides in 10 p.c. hydrochloric acid: 1000 pts. saturated solution contain 10·41 pts. of the salt.

Lanthanum acetate $La(C_2H_3O_2)_3,1\frac{1}{2}H_2O$, thin prisms, furnishes in the cold with ammonia a gelatinous precipitate of basic acetate, which, when mixed with solid iodine, becomes blue like starch iodide. This reaction, which does not occur with the nitrate or with the precipitate from boiling solutions of the normal acetate, depends on the colloidal nature of the basic salt, the colour being due to an adsorption compound. Although this coloration is used as a test for lanthanum it is uncertain so long as other elements are present (Biltz, Ber. 1904, 37, 719).

Lanthanum oxalate $La_2(C_2O_4)_3$, 9, 10, or $11H_2O$, a white curdy precipitate becoming crystalline; is more soluble in acid or in aqueous ammonium oxalate than the oxalates of other rare earth metals (*cf.* Cleve, Bull Soc. chim. 1874, [ii.] 21, 196; Power and Sheddon, J. Soc. Chem. Ind. 1900, 19, 636; Brauner and Pavliček, Chem. Soc. Trans. 1902, 81, 1243). Whittemore and James, J. Amer. Chem. Soc. 1912, 34, 1168.

Lanthanum acetylacetonate $La(C_5H_7O_2)_3$, colourless needles, m.p. 185°, crystallises from water with $3H_2O$ (Annalen, 1902, 323, 26; 1904, 331, 334).

Lanthanum dimethyl phosphate

$$La_2(Me_2PO_4)_6,4H_2O$$

white, hexagonal crystals. solubility in water 103·7 pts. per 100 at 25° (Morgan and James, J. Amer. Chem. Soc. 1914, 36, 10).

For other organic salts of lanthanum, see Rimbach and Schubert, Zeitsch. physikal. Chem. 1909, 67, 183; Erdmann and Wirth, Annalen, 1908, 361, 190; Holmberg, Zeitsch. anorg. Chem. 1907, 53, 83; Jantsch and Grünkraut, *ibid.* 1913, 79, 305; Armstrong and Rodd, Proc. Roy. Soc. 1912, 87, 204; James and co-workers, J. Amer. Chem. Soc. 1911, 33, 1330; 1913, 35, 127; 1913, 35, 872; 1914, 36, 10; 1915, 37, 2652.

Spectra of lanthanum.—Spark and Arc Spectra, *v.* Exner and Haschek, Die Wellenlangen der Bogenspektra, I. and II. 1904; Rowland, A Preliminary Table of Solar Spectrum Wave Lengths, 1896.

Unless rendered impure by the presence of traces of other rare earths, lanthana and lanthanum salts do not become luminescent *in vacuô* under the influence of cathode rays.

G. T. M.

LANTHOPINE *v.* OPIUM.

LAPACHOL. This colouring matter has been obtained from the wood of the Lapacho tree, from Greenheart wood, and also from Bethaberra wood. It was from the first-named that Arnaudon (Compt. rend. 1858, 46, 1154) originally obtained it by extracting the wood with alcohol, and recrystallising the product from a mixture of alcohol and ether. Stein (J. pr. Chem. 99, 1) showed that the same colouring matter was present in Greenheart wood, whilst Green and Hooker (Amer. Chem. J. 11, 267) obtained it from Bethaberra wood.

According to Paternò (Gazz chim. ital. 12, 337; 21, 374) the colouring matter is best extracted from the wood by means of soda solution (1 gram soda crystals in 16 grams water for 20 grams finely divided wood), the product being precipitated from the combined extracts by means of hydrochloric acid, purified by extraction with barium hydroxide solution and reprecipitation with acid. The product thus obtained when recrystallised from benzene is readily obtained in a pure condition.

Lapachol $C_{15}H_{14}O_3$. The m.p. of the crystalline product has been variously stated as 138°C. (Paternò) and 140·5°C. (Green). It is insoluble in water, but soluble in alkalis, yielding red solutions which contain its salts. It is not very soluble in ether, but easily soluble in chloroform, glacial acetic acid, and in hot alcohol or benzene.

Monoacetyl derivative $C_{15}H_{13}O_3Ac$, yellow prisms, m.p. 82°–83°C., is prepared by the action of acetic anhydride and sodium acetate on lapachol. It is insoluble in water, crystallises from alcohol and is very easily hydrolysed; cold nitration converts it into *nitro-acetyl-lapachol* $C_{15}H_{12}O_3(NO_2)Ac$, m.p. 166°–168°C., whilst further acetylation yields a *diacetyl-derivative* $C_{15}H_{12}O_3Ac_2$, colourless crystals, m.p. 131°–132°C.

Various salts of lapachol have been described, of which those of the metals are red in colour, those of organic bases yellow to orange. The sodium and potassium salts crystallise with $5H_2O$: $C_{15}H_{13}O_3Na(K),5H_2O$; the calcium, or strontium salt has only $1\frac{1}{2}H_2O$:

$$(C_{15}H_{13}O_3)_2Ca(Sr),1\tfrac{1}{2}H_2O$$

whilst the barium salt has $7H_2O$:

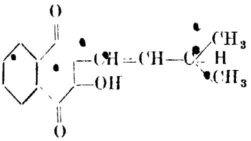
$$(C_{15}H_{13}O_3)_2Ba,7H_2O$$

Anhydrous lead, silver, and ammonium salts have also been described. Of the salts of organic bases, the aniline salt $C_{15}H_{14}O_3{\cdot}C_6H_7N$ consists of yellow needles, m.p. 121°–122°C., that of *p*-toluidine $C_{15}H_{14}O_3{\cdot}C_7H_9N$ of orange-yellow leaflets, m.p. 130°C., and that of *o*-toluidine $C_{15}H_{14}O_3{\cdot}C_7H_9N$ of yellow crystals, m.p. 135°C.

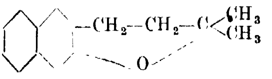
The elucidation of the constitution of this colouring matter is due to Paternò (Gazz. chim. ital. 1883, 12, 337, 622; 1890, 19, 601; 1891, 21, 374); and Hooker (J. Chem. Soc. 1892, 61, 611; 1896, 69, 1355).

It was Paternò who first put forward a structural formula for lapachol, which he based chiefly upon evidence obtained from examination of its oxidation and reduction products.

When oxidised by nitric acid (sp.gr. 1·38), lapachol gives rise to phthalic acid in good yield, whereas when the colouring matter is reduced by means of hydriodic acid and red phosphorus, a substance is obtained which Paternò considered to be β-isoamyl-naphthalene. As the result he suggested the following constitution for lapachol:—

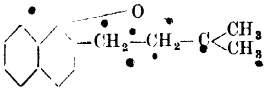


The position of the double bond has been disputed by Hooker. This author concludes that the product which Paternò considered to be β-isoamyl-naphthalene in reality consists of a mixture of two substances to which he gives the names α- and *β-lapachan*, and formulates thus:—



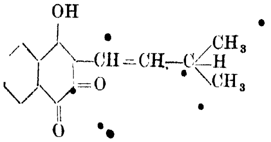
α-Lapachan.

and



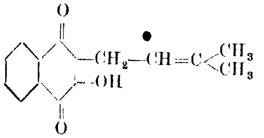
β-Lapachan.

He was able to show that the product obtained by treating naphthalene with isoamyl-chloride, in the presence of aluminium chloride, was not identical with that obtained by Paternò by the reduction of lapachol. Moreover, by condensation of *β-hydroxy-α-naphthoquinone* and *isovaleric aldehyde*, in the presence of hydrochloric acid, he obtained a compound that should have the structure applied to lapachol by Paternò, though to this, in view of its bright red colour, he assigned the formula—

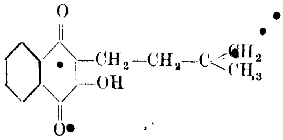


and the name *iso-β-lapachol*.

Although iso-β-lapachol is a derivative of β-naphthoquinone, whilst Paternò's formula for lapachol represents it as a derivative of α-naphthoquinone, both substances should yield the same reduction product, but as the reduction product given by *iso-β*-lapachol is not identical with that obtained by Paternò from lapachol, Hooker concluded that lapachol has in reality the structure—

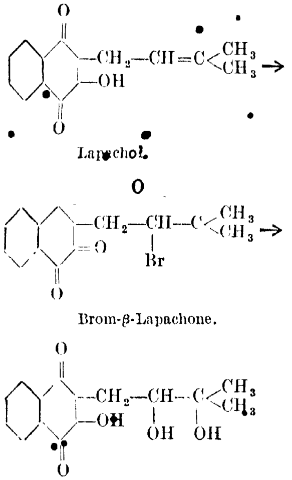


The alternative form—



was rejected by Hooker, and a consideration of the following series of changes makes clear his ground for this rejection.

When lapachol is brominated, in chloroform, the product is *brom-β-lapachone*, orange-red crystals, m.p. 139°–140°C. This when boiled with caustic soda yields *dihydroxy-hydro-lapachol*, m.p. 181°–182°C., and, according to Hooker, on treatment of this product with concentrated sulphuric acid the products (1), (2), (3), and (4) are formed simultaneously, and the changes may be represented by the following scheme :—

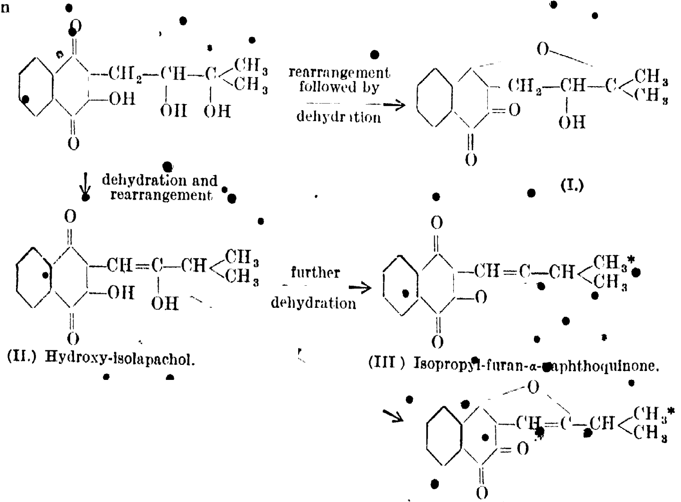


Lapachol.

Brom-β-Lapachone.

Dihydroxy-hydro-lapachol.

Then


rearrangement followed by dehydration
dehydration and rearrangement
further dehydration

(I.)

(II.) Hydroxy-isolapachol.

(III.) Isopropyl-furan-α-naphthoquinone.

(IV.) Isopropyl-furan-β-naphthoquinone.

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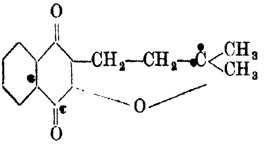
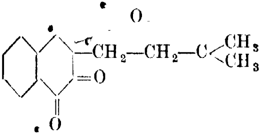
* Both of these substances can be reconverted by the action of caustic soda into dihydroxy-isolapachol though Hooker did not succeed in isolating this as an intermediate product in the initial reaction with sulphuric acid.

When lapachol is treated with mineral acids, Hooker obtained two substances which he termed α- and β-lapachone, and to which the following constitutions have been assigned:—



and

α-Lapachone.



β-Lapachone.

The former consists of pale yellow crystals, m.p. 117°C., and changes on solution in concentrated sulphuric acid into the latter, which forms orange-red crystals, m.p. 155°–156°C.

According to Crosa and Manuelli (Atti R. Accad. Lincei. 1895, ii. 250), Lapacho wood, on prolonged distillation with steam, yields a volatile crystalline product to which they gave the name *Lapachonone*, and composition $C_{16}H_{16}O_2$ colourless crystals, m.p. 61·5°C. It is optically active; its picrate

$$C_{16}H_{16}O_2{\cdot}C_6H_2(NO_2)_3OH$$

m.p. 145°C.; on recrystallisation from alcohol forms products in which the proportion of picric acid is variable.

From lapachonone, by oxidation with dilute nitric acid, they obtained phthalic acid, whilst by the action of phosphorus pentachloride it was converted into *dichlor-lapachonone* $C_{16}H_{14}Cl_2O_2$ large colourless prisms, m.p. 108°C., volatile with steam.

Bromination of lapachonone, in cold acetic acid solution, yields *brom-lapachonone* $C_{16}H_{15}O_2Br$ colourless prisms, m.p. 126°C., together with small quantities of a *brom-dihydroxy-compound* $C_{15}H_{15}O_4Br$, yellow prisms, m.p. 140°C., which forms almost the whole product when lapachonone is brominated in aqueous suspension. It yields a *diacetyl-derivative*, yellow plates, m.p. 132°C., and a phenylhydrazone, red crystalline crusts, which has no definite melting-point (Manuelli, Atti R. Accad. Lincei. 1900 (v.), 9, ii. 314).

A. G. P.

LAPIS-LAZULI (Ger. *Lasurstein*; Fr. *Outremer*). An opaque precious stone valued for its rich deep blue colour. It takes a good polish, and is much used for small ornaments and for inlaying. Formerly it was the only source of the then valuable pigment ultramarine, which is now manufactured on a considerable scale.

Rather than being a simple mineral, it is a mixture of minerals, amongst which the members of the sodalite group predominate, together with calcite, pyroxene, amphibole, mica, scapolite, felspar, iron-pyrites, &c. The material is really an impregnation of various secondary minerals in a crystalline limestone, and has been formed by the contact-metamorphism of calcareous rocks at their junction with granite. The minerals of the sodalite group have been investigated by Brögger and Bäckström, and for the predominant blue constituent of lapis-lazuli they proposed the name *lazurite* (Zeitsch. Kryst. Min. 1890, 16, 231). This is a sodium aluminium silicate and sulphide, and is essentially the same in composition as artificial ultramarine. The formulæ they give for the members of the sodalite group are:

Sodalite $Na_4(AlCl)Al_2(SiO_4)_3$
Haüynite $(Na_2,Ca)_2(NaSO_4{\cdot}Al)Al_2(SiO_4)_3$
Noselite $Na_4(NaSO_4{\cdot}Al)Al_2(SiO_4)_3$
Lazurite $Na_4(NaS_3{\cdot}Al)Al_2(SiO_4)_3$.

An analysis by Brögger and Bäckström of lapis-lazuli from Central Asia gave:

SiO_2	Al_2O_3	CaO	Na_2O	K_2O	SO_3	S	Cl	Total
32·52	27·61	6·47	19·45	0·28	10·46	2·71	0·47	99·97

Here, as in all other analyses, sulphate and chloride are present in addition to sulphide, and, in fact, the haüynite molecule actually predominates in this case.

Lazurite is decomposed and decolorised by hydrochloric acid, with the separation of gelatinous silica and evolution of hydrogen sulphide. It is occasionally found as deep-blue crystals with the form of the rhombic-dodecahedron; sp.gr. 2·38–2·42; hardness 5½.

The best quality of lapis-lazuli comes from Badakshan in Afghanistan; the mines here were visited by Marco Polo in the year 1271. Another occurrence of importance is at the western end of Lake Baikal in Siberia; here the material varies in colour from deep blue to light blue, violet, and green. Large blocks of pale blue lapis-lazuli are also found in the Chilean Andes, and small crystals in the ejected limestone blocks of Monte Somma, Vesuvius.

L. J. S.

LAPPACONITINE *v.* ACONITINE.

LARCH TURPENTINE *v.* OLEO-RESINS.

LARD. The term 'lard' was originally used to denote the fat rendered from the leaf of the pig, *i.e.* the fat from the kidneys and the bowels. The increased consumption of lard during the latter half of the last century (which has seen the rise of large American packing houses manufacturing lard on an enormous scale) has chiefly contributed to the extension of the above definition of lard, so that at present 'lard' denotes the fat from any and every part of the hog.

Leaf lard is still being sold on a small scale as 'butcher's lard' and 'home-rendered lard,' but the amount is insignificant in comparison with the enormous quantities produced in the slaughter-houses of the United States and Canada. The term 'bladder lard,' so named from the package, used to be leaf lard rendered in small establishments. At present this term is still used to denote the best quality of home rendered, as also of American lard, of the quality (*c*) (*v. infra*). The commercial quality 'keg lard' contains, besides leaf lard, the fat taken from other parts of the animal. This extension of the term 'lard,' viz. that it denotes the fat taken from any and every part of the hog, has been implicitly acknowledged by the Adulteration Laws of the United States, according to which lard is defined as the 'rendered fat from slaughtered, healthy hogs, free from rancidity and containing no more than 1 p.c. of substances other than hog fat.'

The production of, and trade in, lard at present may be considered as being completely dominated by the processes and trade usages in vogue in the United States, especially in the large packing houses of Chicago.

The rules of the Chicago Board of Trade define the following brands of edible lard: (*a*) Neutral lard No. 1; (*b*) Neutral lard No. 2 ('Imitation neutral lard'); (*c*) Leaf lard; (*d*) Choice lard, choice kettle-rendered lard; (*e*) Prime steam lard. These brands will be described here in the order in which they are produced in the factory, so as to give, at the same time, a concise account of the manufacturing processes involved in the production of edible lard.

(*a*) **Neutral lard** is prepared from the leaf, which is taken out of the animal immediately after it has been slaughtered, freed from the flesh and skin, and chopped up in a fat-cutting machine into small lumps, which are thoroughly washed with iced water. The comminuted mass is then delivered into jacketed rendering vessels, in which it is heated up to a temperature of 40°–50°. The lard so obtained is practically neutral, and is used almost exclusively in the manufacture of margarine (termed in America 'oleomargarine').

(*b*) **Neutral lard No. 2** ('Imitation neutral lard') is the fat taken from the back, and rendered in a similar manner.

As the Neutral lard No. 1 and Neutral lard No. 2 are not 'cooked' (*i.e.* not rendered at a higher temperature than 50°), these lards do not keep well, and cannot, therefore, be used, like 'leaf lard' and 'steam lard,' for domestic purposes.

(*c*) **Leaf lard** (**'Flare lard,' 'Flair lard'**). When the residue from (*a*) is subjected to steam heat under pressure in a digester, the leaf lard of commerce is obtained. Formerly this was the only kind of lard recognised by the Chicago Board of Trade, and was prepared from the whole leaf, and thus embraced the three qualities described under (*a*), (*b*), and (*c*). This lard is not exported, but is consumed at home. The Adulteration Laws of the United States now define leaf lard as 'the lard made from the internal fat of the abdomen, excluding that adhering to the intestines, and having the iodine number 60.'

The portions of the leaf remaining after the rendering of Neutral lard No. 1, are put together with the residues obtained in the preparation of Neutral lard, and 'rendered' by steam heat in open steam-jacketed kettles or in autoclaves (digesters).

Thus (*d*) **'Choice lard'** or **'Choice kettle-rendered lard'** is obtained. The latter term is due to this fat being rendered in steam-jacketed kettles, which represent the survival of the old-fashioned open kettles, in which butchers used to render the lard over free fire. Such lard has the peculiar, pleasant flavour of fried fat, and therefore the name 'Kettle-rendered lard' has been retained, even after the rendering over free fire had given way to heating by means of steam. In large establishments the rendering is carried out under pressure in digesters. The regulations of the Chicago Board of Trade define 'Choice lard' as lard made from leaf and trimmings only, either steam or kettle rendered. The manner of rendering is branded on each tierce. Its flavour is much superior to that of 'Prime steam lard.'

(*e*) **Prime steam lard**, also termed 'Standard prime steam lard,' is obtained from any trimmings not used up in the production of lard (*d*), and all other parts of the hog that will yield lard, with the exception of the liver, lungs, the intestines proper, and that part of the heart which is free from fat. This quality is rendered in digesters in a similar manner to lard (*d*). Such lard is passed solely on inspection, and as the inspector has no authority which enables him to supervise rendering establishments, in order to secure a proper control, we may take it that prime steam lard consists of the fat from any part of the hog, either from the whole animal, or from portions of it (head, foot, &c.).

The foregoing qualities represent the commercial qualities of *edible* fat.

All those parts of the hog which have not been used for the production of the above qualities are worked up in autoclaves, in order to obtain the last portion of the fat they contain. The fat so recovered is termed 'Yellow grease.' With this yellow grease are mixed all the refuse fats resulting in the course of rendering the edible qualities. 'Yellow grease' is also obtained from the fat rendered from all the animals that have died in the 'stock-yards.' If in the working up of animals which have died in transit, the intestines, &c., have been removed, a whiter quality of fat is obtained. This is sold as 'white grease' for manufacturing purposes. A lower kind of grease than the 'Yellow grease' is 'Pig's foot grease,' a by-product obtained in the glue department of the rendering houses. This 'Pig's foot grease' finds an outlet in the manufacture of low class lard oil and of soap.

The two qualities of 'Neutral lard' hardly require refining. After the clear melted lard has settled in the jacketed vessel, it is run off into a receiving tank, in which the last traces of water and any fibres are precipitated by sprinkling salt over the fat. In fact, this part of the manufacture is closely similar to the processes employed in the preparation of 'Premier Jus.' The settled lard is then immediately ready for use in the manufacture of margarine—which is mostly produced in the same works,—or is run into tierces for shipment.

The next qualities of edible lard usually undergo a somewhat more complicated process of refining, consisting in treating the melted fat in a refining vessel with fuller's earth, and blowing it at the same time with air. The fat is thereby also deodorised. It is next pumped through a filter press, from which the clear, bleached lard is run over horizontal cylinders cooled by brine. The warm lard is thus quickly chilled on the cooled surface of the lard cooler, and forms a continuous sheet of solidified fat. Before the cylinder dips again into the warm lard on the other side, the solidified mass is removed by a scraper ('doctor'), and falls into a trough. In this trough a rotating screw conveyer breaks up the sheet of fat and carries it forward into a mixer, in which the lard is agitated by a mechanical arrangement. Here 'lard stearine' is added to 'stiffen' the lard, in case it be too soft.

The lard stearin is obtained by subjecting cooled lard in hydraulic presses to a moderate pressure, when the softer portion—lard oil—exudes. The lard stearin either serves in the manufacture of butter substitutes (margarine, 'oleomargarine'), or is used, as described above, for 'stiffening' soft lard. In this country, where the addition of beef fat for 'stiffening' lard is now forbidden, considerable quantities of lard stearin are used.

Leaf lard is the hardest; the lards from the back, &c., are softer. The consistence of the lard depends not only on the part of the animal from which it has been taken, but also, and chiefly, on the food which has been given to the animal. Hogs fed exclusively on acorns or on 'tankage' yield a harder lard than hogs fed on maize.

Leaf lard has a granular texture, and a salve-like consistence, and should be of pure white colour. The lards which represent mixtures from all parts of the body, especially those manufactured in large slaughter-houses, have no longer a crystalline texture, as the object of the last operation in the manufacture is to destroy such texture and give to the product a smooth appearance.

The lard rendered from the leaf, as also from the back, has an agreeable taste. The lower qualities have an insipid taste; this disappears, however, on standing. Some of the steam lards have an 'animal flavour,' which may be judged by an inexperienced person to indicate admixture with tallow or 'beef stearine.' This flavour also disappears on standing or on warming.

Lard consists of the glycerides of lauric, myristic, palmitic, stearic, and oleic acids, and small quantities of linolic acid (and perhaps also of linolenic acid). The proportion of stearic acid determined in a number of commercial lards, varied from 6 to 24·91 p.c.

The analytical differences between lards from different parts of the hog are best expressed by their iodine values. Since important differences exist between North American and European lards, chiefly and almost solely owing to the mode of fattening, it is important to note that American lards have considerably higher iodine values than lards obtained in Europe. The iodine values of the latter range, as a rule, between 46 and 60 The iodine value of American lard reaches, however, higher figures than 60, and may even exceed 70.

Lard (like butter and olive oil) used to be adulterated on the largest scale. Beef fat, beef stearin, cotton seed oil, cotton seed stearin, and other vegetable oils, amongst which during the last few years coconut oil and palm kernel oil predominate, are the adulterants most frequently employed. Such admixtures had been for a long time an openly acknowledged practice in the United States of America, and such expressions as 'refined lard,' 'compound lard,' and 'lard compound' were used to designate a mixture of lard with vegetable oil, chiefly cotton seed oil, and cotton seed stearin. At present, however, the restrictions imposed by law have become much more stringent, and lard exported from the United States under official supervision, may be accepted as guaranteed pure, that is, free from admixture with another animal or with a vegetable fat.

The detection of adulterants in lard plays a most important part in the practice of the public analyst. It is impossible here to follow the various practices of the adulterators of lard and follow up such adulterations through their several stages. The reader must, therefore, be referred to Lewkowitsch, Chemical Technology. It may, however, be pointed out that the chief characteristics which the analyst must determine are: specific gravity, melting-point, iodine value of the fat, iodine value of the liquid fatty acids, and amount of unsaponifiable matter. The proportion of the latter is important, inasmuch as admixture of paraffin wax with lard (which had been practised to a considerable extent in former years, and had then been abandoned) appears to have been resumed during the last few years. Modern methods of chemical analysis have rendered the detection of vegetable oils and fats added fraudulently to lard, a somewhat easy process, as the phytosteryl acetate test permits the detection of even as little as 1 p.c. of admixed vegetable oil or fat, and the endeavours of the adulterator to circumvent this test by the addition of a very small quantity of soft paraffin wax have been frustrated by more refined methods of chemical analysis. The detection of coconut oil and palm kernel oil is rendered (in addition to the phytosteryl acetate test) somewhat easy by the determination of the volatile fatty acids. In this connection, however, a note of warning must be sounded, as it has been shown that hogs fed on copra (as is done in the Philippine Islands) furnish a lard which exhibits the characteristics of lard adulterated with coconut or palm nut oil (the coconut oil having been pushed forward into the body fat, much as feeding cows with oil cake leads to the pushing forward of the vegetable oil into the milk fat). Detection of added beef fat or beef stearin to lard is more difficult, and the (formerly relied upon) Belfield test, which was supposed to rest on the detection of (beef) stearin, has been shown to be entirely nugatory. The so-called Stock-Belfield test, which aimed at a quantitative determination of added 'beef stearin,' has been shown to be utterly fallacious, inasmuch as the crystals, on the isolation of which reliance was placed, are given by the lard stearin itself. A method proposed by Polenske, viz. to determine the so-called 'difference' between solidifying- and melting-points has been shown to be untrustworthy.

A method which has given better results is that based by Bömer (Zeitsch. Nahr. Genussm. 1913, 26, 559; 1914, 27, 153) upon the facts that the distinctive glyceride of lard, α-palmito-distearin, shows a difference of 5·2° between its m.p. and that of its separated fatty acids, whereas in the case of β-palmito-distearin, the distinctive glyceride of beef and mutton fats, the difference is only 0·1°. In the case of lards melting between 61° and 65° the m.p. of the glycerides added to twice the difference between the m.p. of the glycerides and their fatty acids should not be less than 71°. In the case of lards melting between 60° and 61° a difference of less than 5° between the m.p. of glycerides and fatty acids indicates the presence of beef or mutton fat or 'hardened' oils, whilst for lards melting between 65° and 68·5° a difference of less than 3° is indicative of adulteration. The value of this test has been confirmed by Sprinkmeyer and Diedrichs (Zeitsch. Nahr. Genussm. 1914, 27, 571), who find that it is capable of detecting 5 p.c. of beef or mutton fat or hydrogenated oils in lard.

By crystallising the fat from acetone and determining the m.p. of the fraction it is possible to ascertain which of the specific glycerides predominates, Vitoux and Muttelet (Ann. Falsificat. 1920, 13, 593), and Bömer's method is then applied to the fraction to obtain quantitative results (*Id.*, Ann. Chim. anal. 1921, 3, 208).

A considerable amount of lard is consumed in the manufacture of lard substitutes.

Lard Substitutes consist chiefly of a mixture of lard, or lard stearin with 'beef stearin' ('oleostearin'), cotton seed stearin, cotton seed oil, maize oil, arachis oil, sesame oil, coconut oil, and palm kernel oil. In the infancy of this industry these artificial products were sold under such names as 'refined lard,' 'commercial lard.' Other products (*e.g.* 'lard compound') contained no lard whatever, being judiciously prepared mixtures of beef stearin and cotton seed oil. At present, however, most lard substitutes proper contain some lard, or at least 'lard stearin,' as a basis, whilst others contain a vegetable oil 'hardened' to the required extent by hydrogenation. The manufacture consists simply in mixing the various fats, in the melted state, and oils in a mixing machine, and cooling the mixture rapidly by running it over cooling cylinders, so as to destroy any tendency to crystallisation.

In order to impart to the finished mixture a pure white colour, it is usual to stir air into the fat until it acquires a salve-like consistence. The stirring with air must not, however, be carried too far, as otherwise the lard substitute not only becomes more liable to rancidity, but easily acquires a foamy consistence. J. L.

LARDERELLITE (*Ammonium borate*). A mineral found in the lagoons of Tuscany. It occurs in small crystalline rhomboidal plates.

B_2O_3	72·06
$(NH_4)_2O$	9·83
H_2O	18·11
	100·00

(D'Achiardi, Chem. Soc. Abstr. 1900, ii. 600).

LASERPITIN, $C_{15}H_{22}O_4$, is a bitter principle, obtained by Feldmann (Annalen, 1865, 135, 236), by extraction of white gentian root (*Laserpitium latifolium L.*) with light petroleum; yield 1·5 p.c. Crystals, m.p. 118°. Alkalis and acids hydrolyse it to angelic acid and resinous *laserol*; *v.* also Külz (Arch. Pharm. 1883, 221, 161). G. B.

LASURSTEIN *v.* Lapis-lazuli and Pigments.

LATERITE. A residual product of rock weathering, met with in tropical regions, consisting mainly of hydroxides of ferric iron and aluminium with intermixed sandy and clayey material. It is reddish-brown with a mottled and streaky distribution of colour, and has a concretionary and cavernous structure. The name, from the Latin *later*, a brick, was introduced by F. Buchanan (Journey from Madras, 1807), on account of the extensive use of the material in India as a building stone. When freshly quarried it is quite soft and easily trimmed into brick-shaped blocks, which harden on exposure. The material forms surface accumulations, up to 30 or 40 feet in thickness, covering rocks of all kinds, particularly igneous rocks (granite, syenite, basalt, &c.) and gneisses, and extending over wide areas in all tropical regions. Whilst in temperate regions aluminous silicate rocks yield on weathering kaolinite and clay products, in tropical regions the silica (of the silicates) is removed together with the alkalis, lime, and magnesia, leaving behind quartz and hydroxides of iron and aluminium. The most abundant aluminium compound is gibbsite ($Al_2O_3 \cdot 3H_2O$), sometimes in a minutely crystalline condition, but more usually in the colloidal form ('kliachite' or 'sporogelite'); diaspore ($Al_2O_3 \cdot H_2O$) is also sometimes present. The iron compounds, including mainly limonite together with turgite and goethite, are also principally in the colloidal form. Hydrated aluminium silicates, kaolinite and halloysite, and the manganese oxides, psilomelane and wad, are also at times present. The alumina present as gibbsite is soluble in hydrochloric acid, whilst that in the clay minerals is insoluble. Being mixtures of all these minerals in varying proportions the composition of laterite consequently varies between wide limits, as illustrated by the following analyses:—

I, laterite overlying nepheline-syenite (also K_2O, 0·27, Na_2O, 0·47 p.c.); II, ditto, overlying diabase; III, ditto, overlying peridotite; I–III, from French Guinea (A. Lacroix, Les latérites de la Guinée, Nouv. Arch. Mus. Paris, 1913, 5, 255). IV and V, the extreme values shown in twenty-two analyses of Indian laterites (H. and F. J. Warth, Geol. Mag. 1903, 154).

	I.	II.	III.	IV. (max.)	V. (min.)
SiO_2	2·21	1·30	12·67	23·32	0·37
TiO_2	0·12	1·03	0·55	6·61	0·01
Al_2O_3	55·83	60·19	12·59	67·88	6·67
Fe_2O_3	5·22	3·91	46·84	56·01	4·09
CaO	0·24	0·17	0·04	0·52	—
MgO	0·19	—	1·26	0·20	—
H_2O	30·47	32·00	15·32	28·10	7·73
Quartz	5·74	1·40	10·73	39·53	—
	100·76	100·00	100·00		

Besides being used as a building stone, slabs of laterite are used in India for the construction of irrigation works. The material grades on the one hand into pure bauxite, and on the other into concretionary iron ores and manganese ores, which sometimes occur as workable deposits. A calcareous variety, containing nodules of calcium carbonate, is used for the manufacture of hydraulic cement and mortar, and the clayey varieties for making tiles.

In addition to the references quoted under the analyses, *see* L. L. Fermor, Geol. Mag. 1911 and 1915; J. B. Harrison, Geol. Mag. 1910; T. H. Holland, Geol. Mag., 1903; H. Arsandaux, Bull. Soc. franç. Min. 1918, 36; G. C. Du Bois, Min. Petr. Mitt. 1903, 22; J. M. Campbell, Mining Mag. 1917, 17. L. J. S.

LAUDANINE, LAUDANIDINE, LAUDANOSINE *v.* Opium.

LAUDANON. A mixture of opium alkaloids.

LAUDANUM. Laudanum is understood in this country at the present day to be the simplest liquid preparation of opium available for medical purposes. The word is an old one, and has undergone considerable change of meaning, but its precise origin has never been ascertained with certainty.

According to some authorities, the term is borrowed from *labdanum* or *ladanum*, an oleo-resin of Greek origin, which is collected from various species of *Cistus* (*v.* Oleo-resins); while others derive the word from the Latin *laus*, praise, which is supposed to indicate the high esteem in which the medicine has always been held. In a discussion of this question (Pharm. J. [iii.] 17, 404, 424, 503, 584, 644), it is pointed out by Eagle that according to Mathiolus (Comment. Dioscoridis Mat. Med. Lugduni, 1563) certain Italians applied the term laudanum to labdanum, and thus Littré and Robin (Dict. Méd. Paris, 1877) and others give the Italian equivalents of the two words as synonymous. This statement of Mathiolus would appear to have been the source of the view that laudanum is derived from labdanum which has been adopted by several lexicographers and writers on materia medica. Hooper (Lex. Med. London, 1848) and Dunglison (Dict. Med. Sc. Philadelphia, 1868) are, however, on the side of the *laus* derivation, and the remarks of such writers as Crollius (Basilica Chymica, Francofurti, 1611), Bruno (Lex. Castello-Brun. Norimbergæ, 1688), Lemery (Pharm. Universelle, 1716), and others are so decidedly in its favour that the weight of evidence at present appears to be with this hypothesis.

But be this as it may, the term 'laudanum' was applied in the 17th century to indicate solid or semi-solid mixtures which generally, though not always, contained opium (*cf.* Lond. Dispensatory, 1678). These were gradually replaced by liquid preparations, of which the most celebrated was that of the physician Sydenham, 1644–1689, whose life was written by Dr. Johnson. This was the *Laudanum liquidum Sydenhami* of the London Pharmacopœia of 1720, and was represented by the *vinum opii* of later medicine. A *tinctura opii* of simpler composition has, however, long taken the lead among galenical preparations of opium. This is a liquid extract made with dilute spirit, and represents in all important respects the physiological activity of the crude drug. To this tincture the term 'laudanum' was applied, both in this country and in the United States, not only by writers such as Pereira (Mat. Med. 1853, 2135) and Stillé and Maisch (Nat. Dispensatory, 1886, 1537), but more especially in the practice of pharmacy. In accordance with the international agreement of 1906, the British Pharmacopœia of 1914 prescribes that *tinctura opii* must contain in 100 c.c. 1 gram of anhydrous morphine. Limit of error ±0·05 gram. The solvent in the finished preparation is 45 p.c. alcohol. The U.S.P. of 1916 has adopted the same limits (*cf.* Opium).

G. B.

LAUREL CAMPHOR *v.* Camphor.

LAUREL OIL. Bayberry oil, is obtained from the berries of the laurel tree, *Laurus nobilis* (Linn.), either by pressing the pounded berries or by boiling them with water. The berries contain from 24 to 30 p.c. of fat. Laurel oil has a green colour; at the ordinary temperature it has a buttery consistence; its taste and aromatic odour are characteristic.

Laurel oil is completely soluble in boiling alcohol; on cooling, crystals of trilaurin separate. Judging from its high iodine value, viz. 66 to 96, laurel oil must contain considerable quantities of olein and perhaps also of less saturated glycerides. From the characteristic numbers which laurel oil gives on analysis, the conclusion must be drawn that the proportion of laurin cannot be very high. The presence of laurin is, however, definitively proved by the fact that on distilling laurel oil *in vacuô*, trilaurin is obtained in the distillate. In the unsaponifiable matter of laurel oil, Matthes and Sander identified melissyl alcohol (myricyl alcohol), phytosterol, and laurane, $C_{20}H_{42}$.

A specimen of the pure oil examined by Fabris and Settimj gave the following values: sp.gr. 0·953; m.p. 32°–33°; Reichert-Meissl value, 5·4; and iodine value, 96·4. The discrepancies in the published values are attributable to the crude oil containing variable proportions of a volatile oil. Laurel oil gives a coloration similar to that given by cotton seed oil in the Baudouin test.

Laurel oil is only used in veterinary practice. It is stated to be adulterated with other fats (lard), coloured green with copper salts.

J. L.

LAUREL WAX. *Myrtle berry wax* (*v.* Waxes).

LAURIC ACID $C_{12}H_{24}O_2$ is present in many vegetable fats, notably in coconut oil, laurel oil, dika fat, and tangkallak fat. It crystallises in needles melting at 43·5°, boils at 176° under 15 mm. pressure, and at 225° under 100 mm. pressure, but cannot be distilled without decomposition at atmospheric pressure. Sp.gr. at 20°/4°, 0·883; $n_D^{20}=1·42615$. It is slightly soluble in hot water, and can be slowly distilled in a current of steam, so that it occupies an intermediate position between the volatile and non-volatile acids. The laurates of alkali metals require much more salt to separate them from their aqueous solutions than the alkali salts of higher fatty acids. For example, sodium stearate can be 'salted' out by the addition of 5 p.c. of sodium chloride, whereas sodium laurate requires 17 p.c. For this reason fats containing a considerable proportion of lauric acid are used in the manufacture of soaps intended for use with sea water. The salts of the heavier metals are only sparingly soluble in water, but are more soluble in alcohol. The methyl ester of lauric acid melts at 5° and boils at 141° under 15 mm. pressure, whilst the ethyl ester boils at 269° at the ordinary pressure. The triglyceride, trilaurin $C_3H_5(O·C_{12}H_{23}O)_3$ crystallises in needles (m.p. 46·4°), and has sp.gr. at 60°/4°, 0·8687; $n_D^{60}=1·44039$. It is readily soluble in ether, but only slightly soluble in cold alcohol.

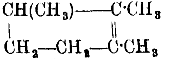
C. A. M.

LAURIN *v.* Laurus nobilis (Linn.).

LAURITE. Sulphide of ruthenium RuS_2, crystallised in the cubic system, probably with parallel hemihedrism and isomorphous with pyrites. The crystals are octahedral in habit with a perfect octahedral cleavage, a dark iron-black colour, and bright metallic lustre. The material is very brittle, H 7–8, sp.gr. 6·99. The only analysis of the natural mineral gave S 31·7[illegible], Ru 65·18, Os [3·03]=100 p.c. (F. Wöhler, 1869); this approximates to the formula $(Ru,Os)_2S_3$, but artificially produced crystals agree closely with RuS_2 in composition. Before the blowpipe it decrepitates, gives first sulphurous and then osmic fumes, and is fusible. It is not attacked by aqua regia or fused hydrogen potassium sulphate, but is decomposed by fused potassium hydroxide and nitrate. It is of rare occurrence as minute octahedra and grains mixed with fine-grained platinum from the platinum washings at Pontijn in the Tanah-Laut district in Borneo; and has also been reported as occurring with platinum in Oregon. L. J. S.

LAUROLENE and *ISO*-**LAUROLENE**, hydrocarbons of the formula C_8H_{14}, first obtained by the distillation of various camphor acids or their salts. (*See* Wreden, Annalen, 1877, 187, 171; Reyher, Inaug-Dissert. Leipzig, 1891, 51; Aschan, Annalen, 1896, 290, 185; Noyes. Amer. Chem. J. 1895, 17, 432; Koenigs and Meyer, Ber. 1894, 27, 3470; Damsky, Ber. 1887, 20, 2959; Moitessier, J. 1866; Walker and Henderson, Chem. Soc. Trans. 1896, 753.)

Laurolene, Δ'-1 : 2 : 3-*trimethyl-cyclo-pentene*,



$$\begin{array}{lll} \mathrm{CH(CH_3)} & \text{——} & \mathrm{C{\cdot}CH_3} \\ | & & \| \\ \mathrm{CH_2{-}CH_2} & \text{—} & \mathrm{C{\cdot}CH_3} \end{array}$$

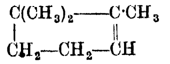
(Eijkmann, Chem. Zentr. 1907, ii. 1208).

Preparation.—(1) By slowly distilling camphanic acid in an atmosphere of CO_2 (Aschan, *l.c.*); (2) by heating sulphocamphylic acid at 170°–180° with aqueous H_3PO_4 (Koenigs and Meyer, *l.c.*); (3) by treating amino-lauronic acid with HNO_2 (K. and M.). Synthesised from $\alpha\delta$-dimethyladipic acid *via* 1 : 2 : 3-trimethyl-*cyclo*-pentanol (Noyes and Kyriakides, J. Amer. Chem. Soc. 1910, 32, 1064).

Properties.—Colourless liquid; b.p. 120°–122°; sp.gr. 0 8097 at 4°/4°, 0·8048 at 10°/10°, 0·8010 at 15°/15°, 0·7974 at 20°/20°, 0·7939 at 25°/25°; mol. mag. rot. 8·987; mol. refraction 61·114 (Crossley and Renouf, Chem. Soc. Trans. 1906, 26); has a sweet odour resembling camphor and turpentine. Rotation very irregular, varies from 0° to +23° and −20°. Combines with 2 mols. Br in chloroform solution; oxidised by HNO_3 to oxalic acid (Crossley and Renouf); oxidised by dilute alkaline $KMnO_4$ to a diketone, b.p. 204° at 750 mm. (corr.), which yields a disemicarbazone, m.p. 194° (corr.) (Noyes and Derick, J. Amer. Chem Soc. 1909, 148, 1609; Noyes and Kyriakides, *ibid.* 1910, 32, 1064; Noyes, *ibid.* 1910, 32, 1068; 1910, 32, 1061). With fuming HI on the water-bath yields *laurolene hydriodide*, a greenish-brown, unstable liquid which, heated with zinc dust in 90 p.c. alcohol, yields *dihydrolaurolene*, 1 [illegible] 3-trimethyl-*cyclo*-pentane, as a colourless liquid, b.p. 111·5°–114° at 760 mm.; unacted on by Br or $KMnO_4$. It has sp gr. 0·7718 at 4°/4°; 0·7670 at 10°/10°; 0·7633 at 15°/15°; 0·7596 at 20°/20°; 0·7567 at 25°/25°; mol. mag. rot. 8·332; mol. refraction 61·138.

For its synthesis *v.* Noyes and Kyriakides *l.c.* It has the structure Δ'-1 : 2 : 3-trimethyl-*cyclo*-pentene (*cf.* Eykman, Chem. Weekblad, 1907, 4, 191; Bredt, J. pr. Chem. 1911, [ii.] 83, 400.

iso-**Laurolene**, Δ^2-1:1:2-*trimethyl-cyclo-pentene*



$$\begin{array}{lll} \mathrm{C(CH_3)_2} & \text{——} & \mathrm{C{\cdot}CH_3} \\ | & & \| \\ \mathrm{CH_2{-}CH_2} & \text{—} & \mathrm{CH} \end{array}$$

(Blanc, Bull. Soc. chim. 1898, 19, 699; Compt. rend. 1906, 142, 1084). Formed by dry distillation of campholytic acid, sulphocamphylic acid, *iso*-campholytic acid, &c. (Walker and Henderson, Chem. Soc. Trans. 1896, 753). Prepared from *iso*-lauranolic acid by heating in sealed tubes for 4 hours at 300° (Blanc, Bull. Soc. chim. 1898, 19, 699); or by distilling with 1½ times its weight of pure anthracene (Crossley and Renouf, Chem. Soc. Trans. 1906, 41). Blanc synthesised it from $\alpha\alpha$-dimethyladipic acid *via* dimethyl-*cyclo*-pentanone (Compt. rend. 142, 1084).

It is a colourless, mobile liquid, with sweet camphoraceous odour; b.p. 108°–108·2° at 742 mm.; sp.gr. 0·7953 at 4°/4°; 0·7907 at 10°/10°; 0·7867 at 15°/15°; 0·7830 at 20°/20°; 0·7795 at 25°/25°; mol. mag. rot. 8·749; mol. refraction 60·565 (Crossley and Renouf). Oxidised by HNO_3 to oxalic acid; oxidised by dilute $KMnO_4$ to dimethyl hexanonoic acid.

$$CO(CH_3)C(CH_3)_2CH_2{\cdot}CH_2{\cdot}COOH,$$

with $HgCl_2$ solution gives a sticky amorphous precipitate. Combines with 2 atoms Br, forming 2 : 3-dibromo-1 : 1 : 3-trimethyl-*cyclo*-pentane, m.p. 80°–85°. Heated at 125° with fuming HI yields the *hydriodide*, which, on reduction with zinc-dust in 90 p.c. alcohol, yields *dihydro*-iso-*laurolene* (1 : 1 : 2-trimethyl-*cyclo*-pentane).

Dihydro-*iso*-laurolene can also be obtained by heating *iso*-laurolene with HI at 200° or with conc. H_2SO_4 (Zelinsky and Lepeschkin, J. Russ. Phys. Chem. Soc. 1901, 33, 549; also 1899, 31, 407). It is a colourless liquid, having a sweet camphoraceous odour, b.p. 113°–113·5° at 7[illegible]0 mm.; sp.gr. 0·7847 at 4°/4°; 0·7800 at 10°/10°; 0·7762 at 15°/15°; 0·7727 at 20°/20°; 0·7694 at 25°/25°; mol mag. rot 8·249; mol. refraction 61·078 (Crossley and Renouf); Blanc, Bull. Soc. chim. 1909, [iv.] 5, 24; Kondakoff and Schindelmeiser, J. Russ. Phys. Chem. Soc. 1911 43, 992.

LAUROTETANINE $C_{19}H_{23}O_5N$ occurs in the bark of *Litsea citrata* (Blume), and in many East Indian lauraceous plants (Greshoff, Ber. 1890, 23, 2546). It crystallises in needles, m.p. 134°, gives crystalline salts, behaves as a secondary amine, contains three ·OMe groups, and probably one hydroxyl group. It exerts a tetanising action in frogs, but is less powerful than strychnine (Filippo, Arch Pharm. 1898, 236, 601).

LAURUS NOBILIS (Linn.). *Bay, Sweet Bay* (*Laurier commun*, Fr.; *Lorbeer*, Ger.).

The classic or noble laurel or bay tree is indigenous to the Levant and is found all along the shores of the Mediterranean. The leaves are used as a flavouring agent, and both the leaves and fruit were formerly employed in medicine.

The fruit, or so-called bay berries, was analysed by Bonastre (J. Pharm. Chim. [ii.] 10, 30) and by Grosourdi (J. 1851, 562). Besides common constituents, bay berries contain *solid and liquid fat*, *volatile oil*, and a *peculiar camphor*. From the fat, Marsson (Annalen, 41, 330) isolated *lauric acid* $C_{12}H_{24}O_2$. It was subsequently found in numerous other fats (*cf.* Heintz, J. pr. Chem. [ii.] 66, 1). Glycerin trilaurate or *trilaurin* $C_3H_5(C_{12}H_{23}O_2)_3$ is associated in the fat with the glycerides of oleic, linoleic, palmitic, myristic, and stearic acids (Staub, Nat. Disp. 1886, 874).

The analytical constants of the expressed oil after being freed from the volatile oil are given by Matthes and Sander (Arch. Pharm. 1908, 246, 165), who have also investigated the resinous unsaponifiable matter which is present in the fatty oil. This was found to contain myricyl alcohol; a *phytosterol* $C_{27}H_{44}O,H_2O$, colourless needles, m.p. 132°–133°; a hydrocarbon, *laurane* $C_{20}H_{42}$, which crystallises from alcohol in slender needles, melting at 69°; and an aromatic unsaturated oily substance.

Bonastre (J. Pharm. Chim. [ii.] 10, 36; 11, 3) was the first to distil a volatile oil from bay berries; yield 1 p.c. It has been studied by Forcke (Arch. Pharm. [ii.] 17, 177); Brandes (*ibid.* [ii], 22, 160); Bley (Rep. Pharm. 48, 96); Gladstone (Chem. Soc. Trans. 17, 3; 25, 1); Blas (Annalen, 134, 1); Wallach (*ibid.* 252, 94); and Bruhl and Muller (Ber. 25, 547). The specimen examined by the last-mentioned investigators distilled between 175° and 275° under ordinary pressure and left a viscid residue. The distillate contained lauric acid, and after treatment with potash and digestion with sodium, yielded a liquid, b.p. 167°–171°. This liquid was found to consist of cineol, pinene, and other hydrocarbons, and is probably the substance described as laurene by the earlier observers. The crude oil also contains large proportions of alcoholic or ketonic compounds which, like menthol or camphor, combine with sodium, the salts so formed being decomposed by water.

Bay camphor or *laurin* $C_{22}H_{30}O_3$ was isolated by Bonastre (J. Pharm. Chim. [ii.] 10, 32) and further investigated by Delffs (J. pr. Chem. [i], 58, 434) and Marsson (Annalen, 41, 329). The yield is about 1 p.c. It consists of prismatic crystals without taste or smell. It is insoluble in water, but soluble in alcohol and ether, and is chemically neutral and indifferent.

The leaves of *Laurus nobilis* also contain a volatile oil, D 0·9215–0·9361; α_D −15·95°; yield 2·4 p.c. Examined by Thoms and Molle (Arch. Pharm. 1904, 242, 161), free acetic, *iso*butyric, and (*iso* ?) valeric acids were found to be present, also about 1·7 p.c. of free eugenol and about 0·4 p.c. of eugenolic esters. The acid obtained by hydrolysing the oil by alcoholic potassium hydroxide consisted mainly of acetic acid; the other volatile acids present were probably valeric and hexoic. A monobasic acid $C_{10}H_{14}O_2$, m.p. 146°–147°, was also obtained. On fractionating the oil, after the removal of the free acids, phenols, and esters, cineol was obtained. The yield of cineol was equal to 50 p.c. of the original oil. From fractions between 212° and 230°, geraniol was isolated. The fractions of a still higher boiling-point contain oxygenated compounds, probably a sesquiterpene alcohol associated with a sesquiterpene. These fractions, and also the original oil, give an intense blue coloration when dissolved in glacial acetic acid and bromine vapour is blown over the surface of the solution.

The volatile oil of the leaves of the allied Californian laurel, *Umbellularia californica* (Nutt.), contains the following substances in approximately the percentages given: eugenol, 1·7; *l* pinene, 6·0; cineol, 20·0; umbellulone, 60·0; safrole, a very small proportion; eugenol methyl ether, 10·0; and traces of fatty acids. *Umbellulone* $C_{10}H_{14}O$ is a colourless oil, boiling at 219°–220° (749 mm.), $[\alpha]_D -37°$, and has an odour somewhat resembling mint. It is a ketone; for constitution and properties *v.* Semmler, Ber. 1908, 41, 3988; *cf.* also Tutin, Chem. Soc. Trans. 1908, 93, 252.

The volatile oils obtained from *Laurus nobilis* must not be confused with others bearing similar names, such as commercial bay oil or bayberry leaf oil (*Oleum Pimentae*, U.S.P.) distilled from the leaves of the West Indian tree *Pimenta acris* (Kostel.), which is the flavouring agent in the toilet preparation known as bay rum (Markoe, Pharm. J. [iii], 8, 1005; Ruse, *ibid.* [iii], 13, 39); laurel oil of Guiana, natural oil of laurel, or ocotea oil, derived from a tree of Spanish Guiana (Stenhouse, Chem. Soc. Mem. 1, 43; 2, 121); or oil of common or cherry laurel, *Prunus Laurocerasus* (Linn.) which is similar to volatile oil of bitter almonds. G. B.

LAUTARITE. Calcium iodate $Ca(IO_3)_2$, crystallised in the monoclinic system. The large (up to 20 grams), colourless or yellowish crystals are prismatic in habit and usually arranged in radiating groups. Sp.gr. 4·59; slightly soluble in water; soluble in hydrochloric acid with evolution of chlorine. The mineral is found in the Chilean nitrate deposits, especially at the Lautaro works near Taltal, where it is often embedded in bands of gypsum. Since these deposits are the principal source of iodine, it is probable that the minerals lautarite and dietzeite (*q.v.*) are there widely disseminated. Crystals of calcium iodate have been obtained artificially from fusion in sodium nitrate. L. J. S.

LAUTH'S VIOLET *v.* AMINES; METHYLENE BLUE.

LAVA. A name of Italian origin applied not only to the molten material poured out on the earth's surface by volcanoes, but also to the same material after its solidification as a volcanic rock. The petrological term *magma* is applied to the molten material itself, whether erupted at the earth's surface or not, and from which igneous rocks of whatever kind have consolidated, including the deep-seated plutonic rocks (*e.g.* granite) as well as the surface lavas or volcanic rocks. Such material consists in all cases mainly of silicates, but with a wide range in composition—from 'acid' to 'basic.' The silica percentage may vary between 80 and 40, the balance consisting mainly of oxides of aluminium, iron, calcium, magnesium, potassium, and sodium, together with some water. In the most acid types (*e.g.* rhyolite) the excess of silica over that required to form silicates is present as quartz,[1] whilst in the most basic types (*e.g.* limburgite) the excess of bases separate out as magnetite and ilmenite, or less often as corundum and spinel. As examples of the extremes in composition of lavas, the following analyses (by J. H. Player) may be quoted: I. rhyolite from C. Antrim; II. limburgite from Haddingtonshire:

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[1] Except, of course, in the case of wholly glassy rocks, in which no minerals have crystallised out.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	H_2O
I.	76·4	—	14·2	1·6	—	0·6	—	4·2	1·8	1·5
II.	40·2	2·9	12·8	4·0	10·4	10·4	11·9	0·8	2·7	3·4

The rocks of the more acid type are paler in colour and lower in density, whilst those of the more basic types are darker and heavier. The former are also much more viscous and less ready to crystallise than the latter. The texture of volcanic rocks depends very much on the conditions under which they have consolidated. When cooling has taken place rapidly glasses are formed (*e.g.* obsidian, *q.v.*, or volcanic glass), whilst if the cooling has been prolonged the whole material may be crystallised. Usually, both glassy and crystalline material are intermingled, the small crystals being set in a glassy base. With the release of pressure accompanying the pouring out of lavas, the water and gases occluded in the magma give rise to vesicular cavities in the mass, in which secondary minerals are frequently segregated. An extreme example of this is afforded by pumice (*q.v.*). Volcanic rocks, representing the lava-flows of ancient volcanoes, occur interbedded with the sedimentary rocks of all geological periods. They find many practical applications, *e.g* as building stones, paving stones, road-metal, concrete, millstones, &c. The leading types—rhyolite, obsidian, pumice, trachyte, andesite, phonolite, basalt—are further described under their respective headings (*q.v.*).

Much detailed petrographical study and numerous chemical analyses have been made of lavas, and many names have been introduced for special varieties. Reference may be made to the text-books of geology (*e.g.* Sir A. Geikie) and petrology (Sir J. J. H. Teall, A. Harker, F. H. Hatch, J. P. Iddings, H. Rosenbusch, and F. Zirkel). *See also* F. W. Clarke, The Data of Geochemistry, Bull. U.S. Geol. Survey, 1908, No. 330; 4th ed. 1920, No. 695. A large number of analyses are tabulated by H. S. Washington, Prof. Paper U.S. Geol. Survey, 1917, No. 99. The lava lakes of Hawaii afford excellent opportunities for the study of molten lava, *see* F. A. Perret, Amer. J. Sci. 1913, vols. 35 and 36; T. A. Jagger, *ibid.* 1915, vols. 39 and 40.

L. J. S.

LAVENDER, OIL OF, *v.* OILS, ESSENTIAL.

LAXANS, LAXATOL, LAXEN, LAXIN, LAXOIN (*Pergen*). Trade names for phenol phthalein when used as a purgative.

LAZULITE. A comparatively rare mineral occurring as sky-blue monoclinic crystals of pyramidal habit. It is a basic phosphate of aluminium, magnesium, and ferrous iron, $Al_2(Fe,Mg)(OH)_2P_2O_8$. This name is easily confused with the name lazurite (*v.* LAPIS-LAZULI). L. J. S.

LAZURITE, *v.* LAPIS-LAZULI.

LEAD. Syns. *Blei*; *Plomb.*; *Plumbum.* Sym. Pb. At.wt. 207·2.

Occurrence.—Native lead is said to have been found at Grassington and Alston Moor, in certain mines in the province of Guanaxuato in Mexico, and according to Koksharow (J. Min. 1875, 873) in the Kirghis Steppe, where it occurs in hornstone associated with heavy spar and cerussite; also in the gold washings of Katharinenburg, in which it occurs in grains together with gold, magnetic and specular iron ores; also in India (Geol. Survey, India, List of Minerals), and in Sweden, where it has been formed from some naturally-occurring compound by reduction with arsenious acid. Some instances of the occurrence of native lead are given by Liversedge, in his Minerals of New South Wales.

A large number of lead compounds are found in nature, but only comparatively few can be considered as ores.

The principal ores of lead in the order of their importance are *galena*, *cerussite*, *anglesite*. Other less important naturally occurring compounds of lead are *pyromorphite*, *mimetite*, *matlockite*, *mendipite*, *phosgenite*, *lead ochre*, *minium*. These are dealt with under special titles.

The association of small quantities of lead with uranium minerals was noted by Hillebrand and made the subject of particular study by Boltwood, who suggested that the lead might be the product of the disintegration of uranium (Amer. J. Sci. 1905, 22, 253; 1907, 23, 77). The development of this idea has led many chemists, in recent years, to the extraction and determination of the equivalent weight of the lead from radio-active minerals (*v. infra*).

Most ores of lead contain silver which may be present either as the native metal or, in the case of sulphide ores, as argentite or some mineral rich in silver, such as tetrahedrite. Oxidised ores (sulphate and carbonate) generally contain silver as halide. The amount of silver varies very greatly; it is usually of the order 0·01 to 0·1 p.c. Some ores, however, especially the sedigenetic ores, are practically free from silver, whilst, at the other extreme, some are so rich as to be regarded as silver ores. Since the silver passes into the lead when the ores are smelted and is almost completely recovered from the lead by the processes of desilverisation and cupellation, and since most of the silver in the world is produced by these methods from argentiferous lead ores, the metallurgy of silver, in so far as this metal is won from lead ores, will be described in the following pages.

Galena is the source of most of the lead of commerce. Its chief modes of occurrence are in veins, more or less vertical and often occupying small fault-fissures; and in flats, or offshoots from veins, usually following roughly the bedding-planes and replacing limestone. Irregular impregnations of porous rocks like sandstone constitute an important source in certain parts of Germany and America. The galena in such cases is usually segregated into nodules, and is remarkably free from silver, and the size of the ore-bodies and the ease with which they can be worked compensates for their low lead-content.

DISTRIBUTION OF LEAD ORES.

In the British Islands, lead ore occurs in rocks of all geological ages from the Ordovician to the Triassic, but it is particularly abundant in veins in the Ordovician and Silurian rocks of Shropshire, Cardiganshire, and Montgomeryshire, of Leadhills and Wanlochhead in Scotland, and of the Isle of Man; and in veins and flats in rocks of Carboniferous (Mountain Limestone) age of Derbyshire, Flintshire, Denbighshire, Northumberland, Durham, and Yorkshire. It occurs also in the granite of Wicklow and the

Isle of Man and in the killas (Devonian) of Cornwall and Devonshire.

In Germany, lead mines are worked in Devonian strata in the valleys of the Lahn and Sieg and in the Hartz. In the latter district there are three centres—viz. (1) that in the neighbourhood of Clausthal; (2) the mines in the vicinity of Andreasberg; and (3) those at Rammelsberg, near Goslar. The Freiberg mines are in gneiss and yield a highly argentiferous galena. The Silesian lead ores are found in irregular deposits in the muschelkalk, and are associated with ores of zinc and iron. A remarkable stratified deposit of lead ore of Triassic age is that of Mechernich in the Eifel, where a bed of sandstone is studded in places with nodules formed of sand grains cemented together by galena.

The mines of Bleiberg and Raibel in Carinthia are among the most important lead mines in Austria. Here the ore is a very pure galena associated with molybdate of lead, and is found in limestones of the Triassic formation. At Pzibram, in Bohemia, the veins are in Silurian strata, and yield a galena very rich in silver. The mines are from three to four thousand feet deep.

Lead is found in almost every province in Spain, the chief workings being those of the provinces Jaen, Murcia, and Almeria. In the province of Jaen in the neighbourhood of Linares, two distinct systems of veins occur traversing the Triassic sandstone and the underlying granite. In the district round Carthagena in Murcia, the lead ores occur in veins in stratified and irregular deposits in Silurian rocks and trachytes. In the province of Almeria lead is found in veins in the mica schists and clay slates of the Sierra Almagrera. Some of the ore of this district is highly argentiferous.

The chief Italian sources of lead are in Sardinia, and may be divided into three types—(1) Ore masses interstratified in Silurian rocks, as in the mine of Monteponi; (2) veins traversing Silurian clay slates, as in the Montevecchio mine, one of the most important lead mines in Europe; and (3) lodes traversing Silurian limestones, *e.g.* Malacalzetta. The ore of the Montevecchio mine consists of galena mixed with blende, iron pyrites, heavy spar, siderite, and copper pyrites. It is poor in silver, whilst that at Malacalzetta carries about 40 oz. of silver to the ton. In Sardinia, the ore is, in all cases, galena. There are numerous deposits of lead ores (galena) on the mainland. In the Brusmipiano mine, in the district of Milan, galena is found associated with cerussite, iron pyrites, jamesonite, copper pyrites, and malachite. At the Morso Alto mine and at the Boltino mine in the mining district of Florence, the galena worked is rich in silver, and at the latter mine is associated with fahlerz, bournonite, and native antimony ore.

The deposits of lead ores in Portugal are very similar to those in Spain. The most important district is that of Mutola, near the Guadiana. The galena contains about 24 oz. of silver to the ton, and the cerussite and anglesite associated with it are frequently much richer.

In Greece, ores of lead, silver, and zinc occur in mica schists, limestones, granites, and trachytes, sometimes in irregular masses and sometimes in the form of lodes. The chief mining district is that of Laurium, at the southern extremity of Attica. The ore has been wrought and smelted there from the earliest times.

In Sweden argentiferous lead ores occur in veins in granular limestones, interstratified with schists. The chief mines are those of Sala, of Lofas in Dalecarlia, and of Guldmenshytta in Westmanland.

In France galena containing silver and associated with blende and iron pyrites occurs at Poullaouen in lodes traversing clay slates of Silurian age. The lodes at Huelgoet yield, in addition to argentiferous galena, cerussite, pyromorphite, and also native silver and horn silver. Galena is found and worked in several localities in France; the most important mines are those of Pontgibaud in the Puy-de-Dôme, where lead lodes are worked which traverse rocks consisting of granite, gneiss, and schists, broken through by dykes of porphyry, and covered by sheets of basaltic lava and beds of cinder. The galena is argentiferous, and is accompanied by blende or iron pyrites, and occasionally fahl ore.

In Belgium, a productive lead mine exists at Bleiberg, near Moresnet, where a vein is worked which traverses the Carboniferous Limestone and the Coal Measures.

Lead ores are found in various parts of Russia, *e.g.* at Ekaterinenburg in the Urals, and in the Caucasus. In Poland there are deposits of galena in the dolomites of the Muschelkalk, which have been worked for centuries. The most remarkable mines are those near Olkusk and Boleslaw. Lodes of lead ores occur near Chasing and Kielcé in rocks of Devonian age. Galena associated with fahl ore, molybdenite, iron pyrites, copper pyrites, and blende occurs in deposits in the mining district of Nertschinsk in Eastern Siberia.

Rich ores of silver and lead occur in the northern Shan States of Burma, and were formerly worked by the Chinese for the sake of the silver. Interest in this source of lead and silver has been revived, the old slags at Bawdwin have been resmelted and ore has been raised in large quantity during recent years.

Australasia.—In Victoria, galena occurs in several localities; that at St. Arnaud is argentiferous. In New South Wales are the famous deposits of Broken Hill, where the galena is intimately mixed with zinc blende. Much cerussite has also been raised from this locality. In South Australia, the mines of argentiferous galena are situated in the southern part of the colony, near Cape Jervis. In the Champion Bay district of Western Australia both lead and copper ores have been found in gneissic rocks. Argentiferous galena has been found in Tasmania, at the Penguin, and in the neighbourhood of Mounts Roland and Claude. Galena containing silver is occasionally found in the gold-bearing reefs of Coromandel and Thames, New Zealand.

Africa.—Argentiferous lead and copper ores are found in some mines in Algeria, and lead ores are known to exist in different parts of South Africa; these ores are found chiefly in the limestone formation extending from the junction of the Vaal with the Orange River in a northerly and then in an easterly direction to Rustenburg, in the north-west of the Transvaal. There is evidence of these ores having at one time been worked by the natives.

America.—In the United States of America, argentiferous galena, associated with blende, iron, and copper pyrites, occurs in the form of veins, in the Atlantic States; in the Azoic slates of New York and in the New England States; in the State of New York it occurs in irregular deposits in the Lower Silurian rocks. The chief lead districts are, however, those of the Upper Mississippi Valley and the Missouri. The Upper Mississippi lead district is comprised within the States of Wisconsin, Illinois, and Iowa, the chief lead-producing district being that of the first-named State. The deposits of lead ore are found in the 'galena' or magnesian limestone of the Trenton period of the Lower Silurian formation, and cover an area of about 140 geographical square miles. These deposits assume a variety of forms, *e.g.* the *sheet*, a solid mass of ore filling a vertical fissure; this is the most characteristic mode of occurrence. In addition, other forms are distinguished, such as an *opening*, *a crevice with pocket openings*, *cave openings*, *flat sheets*, and *vertical openings*, in all of which masses of lead ore occur in fissures in the limestone. The principal ore is a very pure galena, poor in silver; it is accompanied by blende and zinc carbonate and a brown iron ore. The chief deposits of the Missouri district are situated in the counties of Washington, Franklin, and Jefferson. The galena is usually associated with iron and copper pyrites, and at the famous Lamotte mine, with nickel and cobalt ores. In Utah and the Western States, large and irregular deposits of highly argentiferous lead ore occur.

In Canada galena is found in several localities around Lake Superior, a remarkable vein occurring at Silver Lake, some six miles northward from Thunder Bay. A finely crystallised variety of galena has been found on the East Main coast of Hudson's Bay, in strata similar to those in which it occurs in the Mississippi district.

In Mexico lead ores are found in the mines at Guanaxuato and La Concepcion, and lodes containing argentiferous galena, quartz and calc spar occur in the mining district of Tatatila and Zomelahuacan.

The lead-production of the world for the year before the great European war (1913) was 1,142,264 metric tons (1 metric ton=1000 kilos =2204 lbs.=0·98 long or ordinary ton). Of this vast quantity no less than 83 p.c. came from the following five countries:—

U.S.A. . . .	396,034	metric tons
Spain . .	203,000	,,
Germany . .	181,000	,,
Australia .	116,000	,,
Mexico . .	55,530	,,

Owing to internal conditions, the Mexican output was only about half the normal during that year. The United Kingdom produced 48,962 metric tons, 30,000 of which were derived from imported ores. The production, in thousands of metric tons, from other countries was: Belgium, 35; France, 28; Austria, 22; Italy, 21; Greece, 18; Canada, 17. Smaller amounts, from 1000 to 3000 tons, were produced by Japan, Hungary, Russia, and Sweden.

For methods of assaying lead ores, *v.* art. ASSAYING.

The following are the methods by which the extraction of lead is effected:—

I. Method of double decomposition, otherwise known as the roasting-and-reaction, or air-reduction process. As the last name implies, air aids in the reduction, and it does so in the following manner:

When galena is roasted at a moderate heat, it is partially converted into the oxide, and a portion is also oxidised to the sulphate; if, after this roasting the temperature be raised, the unaltered galena reacts on the lead oxide and sulphate formed in the previous stage, and metallic lead is produced, sulphur dioxide being evolved.

These reactions are represented by the following equations:

$$(a)\begin{cases}2PbS+3O_2=2PbO+2SO_2.\\ PbS+2O_2=PbSO_4.\end{cases}$$
$$(b)\begin{cases}PbS+2PbO=3Pb+SO_2.\\ PbS+PbSO_4=2Pb+2SO_2.\end{cases}$$

The second equation must be regarded as a summary one, since there is no evidence of the direct oxidation of lead sulphide to sulphate. Probably all the lead sulphate arises from reaction of lead oxide and sulphur trioxide, the latter being produced by oxidation of sulphur dioxide.

The reversibility of the reactions under (*b*) was indicated by Jenkins and Smith (Journ. Chem. Soc. 1897, 71, 666) in their study of the action of sulphur dioxide on lead. Each equation represents a system of three components in four phases and is thus univariant. The pressure of the gaseous phase, when equilibrium is attained, should thus be a function of the temperature. This deduction from the phase law was confirmed by Schenck and Rassbach (Ber. 1907, 40, 2185, 2947; 1908, 41, 2917).

The interpretation of the data of experiment is, however, rendered difficult by the formation of basic sulphates, which increases the number of phases present and disturbs the equilibrium (*see* W. Reinders, Proc. K. akad. Wetensch, 1914, 17, 703). Some idea of the pressure at equilibrium of the sulphur dioxide for the reaction between sulphide and sulphate may be gained from the following table:

Temp. (degrees centigrade).	Pressure (mm. mercury).
600	39
635	98
665	201
695	402
713	590
723	735

The reversible reaction between sulphide and oxide, viz. $PbS+2PbO=3Pb+SO_2$, becomes appreciable at a temperature (650°C.), about 100° higher than that between sulphide and sulphate, and similar gaseous pressures are attained at correspondingly higher temperatures.

II. Method of roasting and subsequent reduction of the oxidised compounds by means of carbon.

III. The precipitation or iron-reduction process, in which iron is used to effect the removal of sulphur.

The treatment of a lead ore frequently requires the use of two, sometimes of all the above processes.

The smelting of lead ores, of which galena is the principal one, is carried out either in reverberatory furnaces, blast furnaces, or shallow hearths. The ore from the mines is dressed and freed as far as possible by mechanical means from the various minerals and gangue material with which it is mixed

SMELTING IN REVERBERATORY FURNACES.

The *Flintshire process* is an example of the method by double decomposition carried out in reverberatory furnaces, which vary somewhat in construction and dimensions.

The following is a description given by Phillips of a *Flintshire furnace*:—

The length of the hearth is usually about 11 feet, and its width 9 feet, and under this is an arched vault, extending the whole length of the bed to the fire-bridge. The hearth is made of slag, moulded into the proper form when in a plastic and semi-fluid state. Towards the centre of the hearth is a depression in which the fused metal accumulates, and at the bottom of this is situated the tap-hole. The fireplace is at one end, and before reaching the cavity of the furnace the flame has to pass over a fire-bridge about 2 feet in width, and from 12 to 14 inches below the arch. At the opposite extremity of the hearth are openings communicating with the flue in connection with a lofty chimney. The fuel is supplied through a door at one end of the fireplace, in addition to which the furnace is furnished with six working doors, about 9 inches by 12, protected by heavy cast-iron frames built into the brickwork and closed by iron plates, which can be easily removed when required. The bottom of this furnace is made nearly level with the doors on one of the sides, but is inclined towards the other in such a way as to be from 18 to 20 inches below the middle door, where it communicates with the tap-hole, beneath which a cast-iron tapping pot is set in the ground. In the top of the furnace is a hopper, from which a fresh charge of ore is let down as soon as that which is being worked is withdrawn.

In working this process, the charge (consisting of 21 cwt. in N. Wales, and from 12–14 cwt. in the north of England) is let down into the furnace, which is still hot from a previous working, and is spread evenly over the surface of the bed of the furnace, care being taken to prevent it dropping into the depression in the furnace-bed or well. During the first hour and a half, the charge is frequently stirred, and the supply of air carefully regulated so that the temperature is kept sufficiently high to ensure the oxidation of a portion of the galena, but not high enough to cause the charge to melt. At the end of this period the doors are closed, the fire is made up, the temperature raised to bright redness, and maintained at this point for about 25 minutes. The charge becomes plastic, and reaction takes place between the unaltered galena and the oxidised compounds of lead, and the metal so formed runs down into the well of the furnace. At the end of this period, the doors are opened to cool the furnace, and when the charge has become as pasty as ordinary mortar, it is pushed back from the well and spread over the higher part of the bed. The doors are again closed and the temperature raised by addition of fresh fuel; in this way the charge is rapidly run down into the well of the furnace, and when this is accomplished, some slaked lime is thrown on to the surface and, by means of a rake, thoroughly mixed up with the charge. Thus the slags and unreduced ore are cooled and rendered sufficiently pasty to allow of their being again removed and spread over the higher portions of the furnace bed, where they are again calcined as in the first operation. This calcination lasts about half an hour. At the end of this stage, the temperature is again raised, and the whole charge is melted down into the well. During this stage it is customary to throw a little coal slack on to the charge. When the charge has collected in the well, some slaked lime is thrown on to it, and the slags pushed back on to the sloping side of the furnace and allowed to drain. The lead which has collected in the well is now tapped, and the slags, technically known as *grey* slags, are withdrawn in pasty lumps through the doors at the back of the furnace. The surface of the metal in the tapping pot is covered by slags and mattes, which retain mechanically a considerable proportion of metallic lead, the separation of which is effected by stirring with a paddle and throwing on to the surface some coal slack, which is well worked up with the molten metal. A considerable evolution of gas takes place; this is ignited, and the heat produced suffices to melt and liberate the metal confined in the slag. The slag is then skimmed off, thrown into the furnace, and the lead ladled out into cast-iron moulds.

Before introducing another charge, the tap-hole is opened to allow the lead produced from the slag and skimmings to run into the metal pot, where it remains until the next charge is run off. The tap-hole is again closed, and another charge of ore dropped into the furnace from the hopper.

This process may, therefore, be summarised as follows:—

(1) Calcination of the ore at a low temperature, whereby a certain amount of lead sulphide is converted into lead oxide and lead sulphate.

(2) Melting down of the charge, during which the unaltered lead sulphide reacts upon the oxidised products and separation of lead occurs.

(3) The admixture of lime with the molten charge and the 'setting up' of the slag; further separation of lead from the interaction of the sulphide and the oxidised compounds of lead, and the production of an excess of lead oxide and lead sulphate over the lead sulphide present.

(4) The tapping of the metal which has accumulated during the operation, and the drawing of the slags in a pasty condition.

In Flintshire, the ores smelted by this method yield 75–80 p.c. of lead by the dry assay, and of this, 90 p.c. is obtained by smelting in reverberatory furnaces, the remaining 10 p.c. being obtained by subsequent treatment of the slags (of which about 4 cwt. per charge is produced) and fume. The time required for the working of the charge is from 5 to 6 hours.

This method is suitable for rich ores containing limited amounts of silica, pyrites, and calcspar. If the silica exceeds 4 p.c. there is danger of fusible lead silicate being formed. Much pyrites leads to the formation of lead matte, and more than 10 p.c. of calcspar diminishes the fusibility of the slags too much.

In Flintshire, another process of extraction was used, similar to that employed at one time in Cornwall, the two stages of oxidation and reduction being performed in separate furnaces. The method is a combination of all the different processes for the extraction of lead, utilising

(1) The air-reduction process,
(2) The desulphurisation of galena by iron,
(3) The reduction of oxidised lead compounds by carbonaceous fuel.

The ore treated in Cornwall was essentially a cupriferous galena containing on the average 60 to 70 p.c. of lead and about 35 ounces of silver to the ton.

The calcination was performed in a reverberatory furnace having three working doors, one on either side of the furnace, and the third on the side opposite the fire-bridge, and smaller than the others. Below the bed of the furnace was an arched chamber, into which the calcined ore was raked through holes in the bed opposite each of the lateral working doors. The furnace was built of ordinary rubble-work, lined internally with 9 inches of fire-brick. The doors were hung in a cast-iron framework, or had the sides protected by slabs of granite. The charge was introduced through a hole in the roof merely closed by a slab. The charge varied from 25 cwt. to 3 tons, but usually consisted of about 2 tons, and was spread over the furnace bed and calcined at a high temperature, regulated so as to prevent clotting. The operation lasted from 15 to 18 hours, the charge being raked over every hour. At the end it was raked through the holes in the furnace bed into the vault below, whence it was conveyed into the flowing or melting furnace, which is similar to the Flintshire furnace.

This furnace had five working doors, a pair on either side, and the fifth on the side opposite the fire-bridge, as in the calcining process. Near one of the lateral working doors, the hearth sloped to the one near the bridge, where the tap-hole was situated, from which the metal, &c., ran into an iron pot placed outside the furnace, near to which was a small pit to receive the regulus or slurry. The metal pot was also provided with a channel to convey away the slag.

The charge of two tons of calcined ore was brought into the furnace through the back working doors, spread over the sloping hearth, the doors closed, and the temperature raised until the charge was melted down, requiring some 2 or 3 hours. With pure ores, the lead produced in this stage was tapped off, but more usually the charge was mixed with lime and culm (anthracite coal) and set up on the higher part of the furnace bed. When barytes was present in the charge, fluorspar was used as a flux, and 1 or 2 cwt. of scrap iron was added to assist in the decomposition of the lead sulphide.

The doors were again closed and luted, and the charge melted down. The furnace was then tapped, and the molten metal flowed into the metal pot, followed by the regulus or slurry, consisting chiefly of iron sulphide and containing most of the copper. The regulus ran over from the metal pot into the pit below, and after a time the slag began to make its appearance; the lip of the pot was then stopped with ashes, and the flow of the slag directed along the channel by which it was conveyed out of the building.

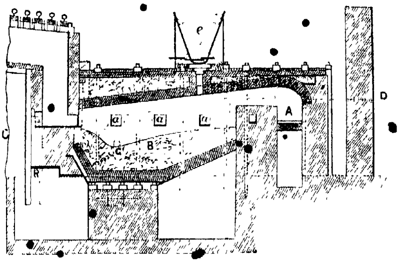

FIG. 1.

The whole operation of smelting, from the time of introducing the charge to the tapping of the metal, took about 8 hours. The slag was generally sufficiently free from lead not to require subsequent treatment. The regulus was treated for the lead and silver it contained, and then when sufficiently rich in copper sold to the copper smelter.

In calcination, 6 cwt. of coal were required for every ton of ore, the melting down requiring about 8 or 9 cwt. The lead obtained was usually hard, and required softening at a high temperature to remove the antimony which it contained.

A modification of the Flintshire process is used at Coueron, Loire Inférieure, France, of which the following is a description taken from Phillips's Elements of Metallurgy. The construction of the furnaces will be understood by reference to the accompanying wood-cuts.

Fig 1. is a longitudinal section.

Fig. 2 is a horizontal section on the line CD.

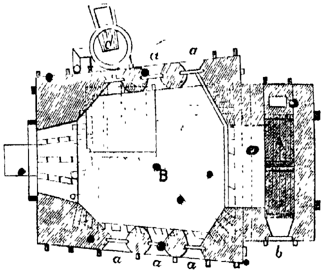

FIG. 2.

Fig. 3 is a transverse section through the tapping-hole.

The fireplace A is of the usual dimensions, and the hearth B, instead of being on an arch, as is commonly the case in North Wales, is supported on iron bars, on which is laid a course of flat tiles. A course of fire-bricks on edge rests on the tiles, and over this is the usual slag bottom. The furnace has the ordinary number of working doors, *a*, with a fire-door *b*, and a tapping-hole *c*; there is a small fireplace below the pot *d*, to prevent the too rapid chilling of the lead during the process of ladling into moulds.

Although similar in form and dimensions to the ordinary Welsh furnace, it differs from it in one important particular, namely, in having the tapping-pot placed near the flue end instead of under the middle door. This arrangement gives a larger surface to the hearth for roasting the charge, and permits of the lead being collected in the coolest part of the furnace, where it is least exposed to loss from volatilisation.

The mode of working varies with the nature and composition of the ores, and depends principally on the length of time required for roasting. Pure ores, especially those containing a notable proportion of lead carbonate or sulphate, require very little roasting, whilst those containing blende, pyrites, &c., must be calcined for a considerable time before smelting.

In general, the ores treated are derived from Sardinia, and contain on an average about 81 p.c. of lead, chiefly galena, carrying but little silver. The cobbled ores, before delivery to the furnace, are ground between rollers and passed through sieves of eight holes to the linear inch. A charge of ore weighs 27 cwt.

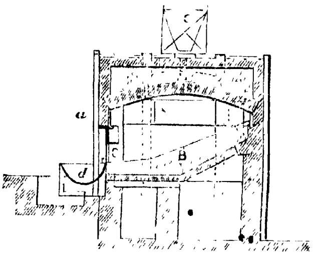

FIG. 3.

Two men are employed at each furnace, one of whom, the chief, works on the fore-side and takes the leading part in the work.

In the treatment of rich ores, the ordinary method of working consists in roasting them in such a manner that more than one-half of the lead sulphide present in the ore is converted into a mixture of oxide and sulphate. On raising to bright redness the oxide and sulphate formed in roasting react on the undecomposed sulphide in the charge, producing metallic lead, sulphur dioxide, and slag.

The process is thus divisible into two well-marked and distinct operations:

I. Calcination or oxidation.

II. Smelting or reduction

I. *Calcination.*—Supposing a charge to have been just worked off and the residual slags withdrawn, the furnace will be empty and at a red heat. The damper having been lowered, the charge of ore in the hopper, *e*, is let down through the opening in the arch, and spread evenly over the furnace bottom by means of rabbles. This done, the working-doors are closed, but the fire-door is left open and the fire damped with cinders, in order so to moderate the heat that the charge may become red-hot without clotting. The charge is thus left undisturbed for some time. During the first hour it is once or twice lightly rabbled; at the expiration of that time, after being well turned with the paddle, it will be found to be red-hot throughout. The damper is then lowered so as to leave just sufficient draught for the free escape of the gaseous products of calcination. The working-doors are now left partially open to admit the air necessary for the oxidation of the galena, and under its oxidising action the charge soon acquires a high temperature. Care must, however, be taken to prevent the heat from increasing so much as to cause softening of the ore. When the heat is properly controlled a white crust, consisting of a mixture of lead oxide and sulphate, in which the former predominates, is rapidly formed on the surface of the charge, and no fumes are visible.

The surface is renewed about every quarter of an hour, either by rabbling or by paddling. The requisite heat is maintained in the furnace during this process by firing with cinders only, which are preferable to coal for that purpose, not merely on account of their lower cost, but also because they give a steadier heat and do not yield gaseous hydrocarbons to interfere with the oxidation.

The alternate raking and paddling of the charge is continued at regular intervals, until on examination, it is thought to be sufficiently desulphurised, which is generally the case at the end of from four to four and a half hours.

The grate is then freed from clinker, coal is thrown on the fire, the damper is opened, and a brisk fire is got up; thus in a few minutes the heat in the furnace is so raised that the reaction-period sets in.

II. *Smelting.*—The ore lying at the back and extreme end of the furnace is now raked towards the bridge. With the increase of temperature, the roasted ore soon begins to soften and to give off white fumes, thus showing that the reactions which result in the liberation of metallic lead have commenced. Great care and attention on the part of the smelter are, however, necessary, in order to prevent too great a loss of lead by volatilisation during the heating up of the charge. The ore must on no account be allowed to liquefy, and as often as it shows a tendency to fuse, some slaked lime in powder is thrown on the charge and well worked into it with a rake. The consumption of lime amounts altogether to about 2 p.c. of the ore treated. By this means, and by carefully regulating the draught and firing, the charge can be heated to the required temperature without fusion.

Shortly after reduction begins, globules of lead may be seen on the surface of the charge, and before an hour has elapsed a certain quantity of lead has drained down the slope of the hearth into the well. The reactions are much aided by frequently rabbling and turning the ore; but as the working doors must remain open for this purpose, a large quantity of air enters the furnace, thus oxidising the sulphide in the ore, and so cooling the charge that the flow of lead is checked. When the cooling is judged to have been carried sufficiently far, the charge is rabbled, the doors closed, and the fire so urged as to fill the furnace with flame during several minutes; then, on re-opening the doors and paddling, the flow of lead recommences.

At the expiration of from two and a half to three hours from the onset of the reaction-period a considerable amount of lead will have accumulated in the well. A first tapping is then made, the lead being received in the tapping-pot, which is kept warm by a small fire, and the tap-hole is stopped with a plug of stiff clay.

The thick dross which rises to the surface of the lead, and contains a certain quantity of sulphide removed from the charge by the hot lead and again separated on cooling, is skimmed off with a shovel and put back into the furnace. A little fine coal, together with some burning cinders and lime, is now thrown on the lead, which is vigorously agitated with a small paddle and stirred until it is clean. It is then skimmed, the skimmings being put on one side and the clean lead ladled into moulds.

The firing, paddling, and cooling of the charge are repeated several times, until at last the residue becomes dry and gives but little lead. Thereupon the heat in the furnace is considerably increased, but not sufficiently to fuse or flow down the charge, and towards the close of the operation the material remaining on the hearth consist to a great extent of oxides.

The pot skimmings, composed of cinders and lead matte, are now thrown into the furnace and well paddled with the charge, the reaction of the lead sulphide and cinders on the oxide and sulphate producing a further yield of lead. When this has ceased and it is seen that no more can be extracted except at a high temperature and by the addition of coal, the grey slag is raked through the middle door at the back of the furnace and the second and last tapping is made.

The whole period of reactions occupies from 5 to 5½ hours. After the withdrawal of the slags, the bottom is examined, and if corroded into holes, or in any way injured, it is repaired by putting into the cavities a mixture of grey slag and lime and beating it smooth with the paddle. It is of great importance to maintain the bottom perfectly smooth and with a good slope on all sides towards the tap-hole. A little lime is now spread over the bottom, and a fresh charge is at once let down into the furnace, the damper having previously been lowered to prevent loss of fine ore by the draught. The weight of coal consumed is equal to 40 p.c. of the ore smelted. The produce of lead per charge of 1350 kilos. of ore (with 81 p.c. of lead) is 15 pigs weighing 901 kilos. and 290 kilos. of slags containing 50 p.c. of lead. Hence the total loss of lead in the reverberatory furnace is 3·52 p.c. by volatilisation; out of this a certain proportion is recovered from the fume collected in the condensers and flues. A larger percentage of lead in pigs might be obtained by adding more coal to the charge towards the end of the process and firing hard, to reduce part of the lead left in the slags. It is, however, considered more economical to limit the production in the reverberatory to about 80 p.c. of the lead contained in the charge, and to carry the richer slags to the blast furnace. This is especially the case when the blast furnace is connected with good condensers and long flues.

It will be seen from the foregoing description that the process of reverberatory smelting adopted at Couëron differs principally from that generally employed in England in that there is no melting or flowing down of the charge, and the period of roasting is greatly lengthened

Spanish furnace or boliche.

In the south of Spain, the smelting of lead ores has been carried on for many centuries in a form of furnace known as the *boliche*. It consists of two chambers, separated from one another by a fire-bridge. One of these only is used for the reduction of the ore, and the second, which is situated between the first and the chimney, serves apparently to moderate the draught.

The fireplace projects from one side of the hearth, and is without a grate; the fuel, consisting of wood, is supplied through a door at the end of the fireplace.

The smelting hearth inclines towards the working door, situated at the end of the longer axis, immediately within which is a receptacle in the floor for the collection of the metal.

The boliche is constructed of rubble work, cemented together by clay and strengthened by buttresses built at the angles.

The interior is lined with fire-brick, and the hearth is made of clay or a mixture of clay and broken galena.

The method of smelting is in principle similar to the Flintshire process. The ore, thrown into the furnace through the working door, is first spread evenly over the surface of the hearth and then calcined. When the calcination is completed, the temperature is raised and the running down of the charge begun. The slags are dried up after the completion of the melting down by throwing into the furnace the ash and breeze from the ashpit. The metal is tapped into a vessel, in which it is stirred with dry leaves, and finally ladled into moulds. The charge consists of 13 cwt. of ore and 1500 to 1750 lbs. of brushwood.

The yield is about 80 p.c. of the lead of the ore as given by the dry assay. The grey slags contain from 45 to 50 p.c. of lead and represent 15 to 17 p.c. of the charge. These slags are subsequently treated in a blast furnace. These furnaces have lately been altered by English companies; coal replaces brushwood as fuel, and the charges have been increased.

Bleiberg process.—At Bleiberg in Carinthia, reverberatory furnaces of a special construction are used, two being usually built side by side and arranged to work into one chimney.

Fig. 4 represents a front elevation, and Fig. 5 a horizontal section. The hearth is about 10 feet long, and at the back near the fire is about 4 feet 10 inches wide. This width is maintained for about half the length of the furnace, when it is gradually reduced, until at the working door it is about a foot wide. The hearth is sloped from the back and also from the two longer sides, thus forming a depression in which the metal may collect and flow into the metal pot, *a*, in front of the working door, *g*.

The hearth is formed of a lower layer of beaten clay and an upper one of fused slags, having a united thickness of about 6 inches. The fireplaces are built parallel to the longer axis of the furnace, and separated from the latter by a fire-bridge. The products of combustion pass into the chimney, *h*, by a flue above the working door. The grate is of stone, having

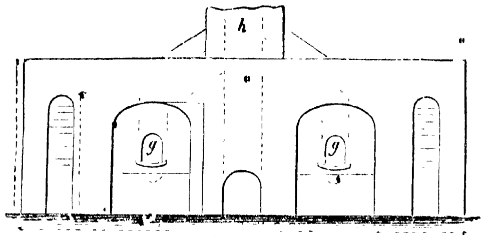

Fig. 4.

greater inclination than the hearth, and is traversed by openings for the admission of air.

The fuel employed is wood, but in some cases brown coal is used, and then the stone grate is replaced by one with iron bars. The lead ores are delivered to the smelter either in the rough state or in the form of slimes. In the former state on assaying they yield from 65–70 p.c. of lead, in the latter from 60–65 p.c.

In smelting, a charge of 375 lbs. of ore is thrown into the furnace through the working door and spread over the hearth, forming a layer from 1 to 1½ inches thick. This is calcined at a temperature low enough to prevent the softening of the charge—the calcination occupying 3 to 4 hours—the charge being raked over at intervals. The temperature is next raised to bring about the usual reactions between the oxidised compounds and the unaltered galena, the charge being carefully rabbled. This operation lasts from 3 to 4½ hours, the metal produced constantly flowing into the depression, and thence to the metal pot. At the end of this operation the slags are dried up by the addition of ashes and breeze, and then withdrawn from the furnace. The lead produced from the ore in this way, amounting from 125 to 150 lbs., is supposed to be specially pure, and is known as '*Jungfernblei*,' or 'virgin lead.' After the withdrawal of the slags a second charge of ore is treated, the slags produced being left in the furnace, and to them the slags from the previous smelting are added. These slags are free from sulphide and contain lead in an oxidised state only. The temperature is raised and charcoal added, the whole being intimately mixed with the rabble. The oxidised lead compounds are in this way reduced in from 7 to 8 hours, about 150 lbs. of lead being produced.

The complete working of the two charges occupies from 21 to 23 hours, the yield of lead being usually about 2½ p.c. below that obtained in the dry assay. This method is now seldom used.

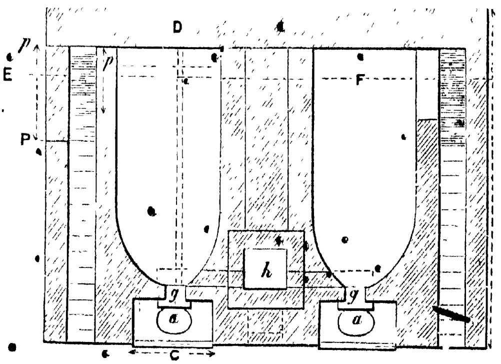

Fig. 5.

Smelting galena with iron in reverberatory furnaces.—When galena is heated with iron, sulphide of iron is formed and lead is liberated. This is the basis of the precipitation or iron-reduction process. The reaction is however, not complete, since some lead sulphide passes into the iron sulphide to form a matte, the amount of lead escaping reduction in this way being greater the lower the temperature. When shaft furnaces are employed, the iron may be charged in the form of oxidised compounds or highly ferruginous slags (*e.g.* tap-cinder), the reduction of which is effected by carbonaceous materials; but with reverberatory furnaces, the iron must be in the metallic condition; the consumption of fuel is large, much lead is volatilised at the high temperature of reaction, and both matte and slag, being rich in lead, require retreatment. Owing to these disadvantages, the reduction is seldom, or never, carried out in reverberatory furnaces.

Smelting in Hearths.

The extraction of lead from galena by smelting in hearths involves essentially the reactions of the air-reduction process. Whereas, however, in reverberatories the stages of roasting and reduction are in the main separate, in hearths they occur side by side. Some reduction, too, of lead oxide by the fuel of the charge takes place in the hearth process. The ore used in this process must contain at least 68 p.c. of lead and should be poor in silver, otherwise the loss of that metal by volatilisation is great. It is broken up small, about the size of a bean, or if very fine is first sintered. The iron of the hearth is protected from corrosion by the lead which fills the sump, and the charge floats on a bath of molten lead and is not itself melted.

The furnace known as the 'ore hearth,' or 'Scotch hearth,' is the one chiefly used in the northern counties of England and in Lanarkshire. It varies somewhat in dimensions and in external form at different works, but consists essentially of a shallow rectangular hearth built of cast iron, set in brickwork or stone. Fig. 6 is a vertical section of the 'ore hearth,' A the hearth bottom, 22 inches square, the iron plate being about 3 inches thick; the sides are also omposed of iron of the same thickness, and the lepth of the hearth is about 4½–6 inches. In ront of the hearth is the work-stone B, sloping rom the front edge of the hearth to the metal ot C, in which the lead is maintained in a molten tate by a fire below. The work-stone is about feet long, 18 inches broad, and 2½ inches thick; t has a raised border about an inch high on its wo sides and along the front, and a narrow hannel 2 inches wide and 1 inch deep runs diagonally across it. The work-stone is embedded n fireclay or a mixture of slime ore and bonesh. At the back of the hearth is a prism of ron, called the back-stone, D, upon which rests he bellows-pipe, and above it is another prism , called the pipe-stone, with an opening below o receive the bellows-pipe. The blast-pipe nters at a height of 6½ inches above the level f the upper end of the work-stone, and when in vork is about 4 inches above the level of the netal in the bed. The hearth is covered by a ood of brickwork, opening at the back into a lue leading to the fume chambers. Behind the earth is a blind flue or pit into which 'hearthnds' and other materials coming off with the ume may be collected, and from which they are emoved as required. At the side of the hood is n opening in the brickwork communicating vith the hearth, through which the ore and fuel re charged. The opening in front can be egulated by a movable iron plate, raised or owered by a counterpoise so as nearly to close he front of the hearth.

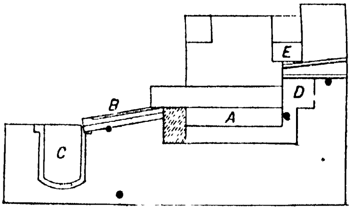

FIG. 6.

The fuel used is either coal or peat, now nore usually coal, and the blast is supplied by a Roots blower, driven by a water-wheel. The nass of agglomerated ore, slag, and coke left at he end of each shift is called the 'browse.' In vorking, a fire of coal is made on the hearth, nd then a moderate blast turned on. Ore is ext thrown on, and when the hearth is provided vith a shutter, this is closed down. After the apse of a few minutes, the charge is stirred by a oker and fresh fuel and ore, and a little lime dded from time to time, the fuel being thrown n front of the tuyere. At intervals the shutter s raised and a portion of the charge drawn on o the work-stone, the grey slags picked out and he remainder broken up and returned to the earth. The charge is rabbled so as to distribute he blast. As the lead is formed it trickles into he well, and overflows along the channel in the vork-stone into the pot in front of the hearth, rom which it is ladled into moulds. Towards he end of a shift fresh ore is not added, but the browse' is thoroughly worked up alone, and vhen the blast is stopped, the grey slags are eparated, and a portion of the lead from the metal pot ladled back into the well so as to fill it for the next shift. Each furnace is attended by two men and produces about a ton of lead on a 6-hour shift. The fuel-consumption is small, amounting to 6–8 p.c., since the oxidation of lead sulphide both to oxide and sulphate is strongly exothermal. The grey slags contain 35–45 p.c. of lead, largely in the form of oxide and sulphate, and are well adapted for smelting in shaft furnaces. The effect of sintering the ore before smelting in hearths is shown by the following results obtained by Cookson, in smelting 400 tons of ore, yielding on assay 81 p.c. of lead, one half of which was smelted raw and the other half after roasting (*v.* Local Government Report, 1878–9. Supplement containing the Report of the Medical Officer, 1878, 289).

	200 tons roasted	200 tons raw
Lead, first fire . .	73·10	60·80
Lead in grey slags .	2·50	1·80
Lead in fume, hearth-ends, loss, &c. . .	5·40	18·40
	81·00	81·00

The ore hearth cannot be worked continuously, as it becomes too hot. Usually, after 8–12 hours' working it has to be laid off to cool. Many devices have been suggested and put into practice in order to overcome this difficulty. The American hearth, first introduced at Rossie, New York, is similar in construction and working to the Scotch hearth, but differs in having the two sides and back formed into an air chest, the air from which is led by a pipe to a tuyere at the back of the hearth. In this way the back and sides of the hearth are kept cool and a hot blast is supplied. The latter has not, however, proved an advantage, for the loss by volatilisation is greatly increased This has led to the replacement of this form of hearth by what is known as the American water-back ore hearth, which has the three sides of the furnace formed of a water-cooled, cast-iron jacket.

A recent modification of the ore hearth, in which mechanical rabbling is successfully employed, is the Newnam or St. Louis hearth. The rabble-arms are hung from a carriage travelling on an overhead track, and their motion is similar to that of the hand-rabble. They work in one direction only, and each time the rabbles are withdrawn from the charge they are carried forward 4 inches by the carriage and are then in position for the next stroke. A 'helper' follows the rabble with a long-handled shovel, pushes back the loose charge and picks out the grey slag; behind him comes a 'charger' who spreads fresh ore and fuel. At the end of a trip, the rabbling machine is returned, without rabbling, to the other end of the furnace, and the operations are repeated.

With this arrangement it has been found possible to double the length of the hearth without increasing the manual labour required to work it; at the same time, the consumption of fuel is halved and the production of fume and dust is greatly diminished. The following results are averages for an 8-hour shift, over a period of 4 weeks, for an 8-foot Newnam and a 4-foot hand hearth worked side by side, the labour being the same in each case. The ore consisted of galena concentrates containing 72·5 p.c. lead and 15·1 p.c. sulphur.

	Newnam hearth.	Hand hearth.
Dry ore charged	13,179 lbs.	5,091 lbs.
Pig lead produced	6,443 „	2,030 „
Grey slag	3,318 „	1,329 „
Dust and fume	2,328 „	1,481 „
Distribution of lead in the products:		
Pig lead	67·44 p.c.	55·00 p.c.
Grey slag	15·18 „	16·20 „
Dust and fume	17·38 „	28·88 „
Consumption of coke breeze	3·6 „	8·8 „
Elimination of sulphur of the charge	87·9 „	80·6 „

It is claimed that the cost of production of lead from rich ores and concentrates by this process is much below that for sintering and blast-furnace smelting (W. E. Newnam, Trans. Amer. Inst. Min. Eng. 1916, 2139).

Slag hearth.—The rich grey slags consisting largely of oxide and lead sulphate, with some unaltered galena, obtained in the air-reduction process, are sometimes smelted in a low-shaft furnace, known as the slag-hearth. This is a shallow, rectangular furnace made of cast-iron plates, open at the front so that the metal and slags flow away continuously, and furnished with a single tuyere. The bottom- or bed-plate slopes to the opening, and is covered with cinders, well beaten down. The hearth bottom thus formed slopes from the back to the open eye of the furnace and serves as a filter to separate the lead from the slags.

In front of the furnace is a forehearth with two iron pots, one for lead, the other for slag. The slag flows over from the first into the second pot, and is there granulated by a stream of water, so that shots of lead, held mechanically by the slag, are liberated.

The charge consists of grey slags and fuel in the form of peat or coke; occasionally, ferruginous materials are added. The chemical changes involved are those of the roasting and reaction process, and reduction by carbon, sometimes combined with precipitation by iron. Grey slags are now usually smelted in the blast furnace with coke and iron slag.

SMELTING IN BLAST FURNACES.

Smelting in reverberatories and hearths is restricted to high-grade ores and concentrates containing over 60 p.c. of lead and less than 5 p.c. of silica. Ores not conforming to this standard of composition, as well as slags from the air-reduction process, roasted mattes and furnace products rich in lead are smelted in the blast furnace. Surface ores, or similar mixtures of sulphide and oxidised compounds of lead, may be smelted direct; ores which consist largely of sulphides must first be roasted to remove the sulphur and convert the lead into oxide (and sulphate), and the roasted product is then smelted with reducing agents, fluxes being added, if necessary, in order to slag the earthy and silicious materials of the charge. If the charge contains much sulphur this is not, as a rule, eliminated under the conditions existing in the blast furnace, but it enters into combination with iron, copper, and lead to form a matte. As the complete removal of sulphur from an ore by roasting (*i.e.* dead-roasting) is a difficult and expensive operation, and as many lead ores contain copper, some cupriferous matte is generally produced in blast-furnace smelting, and from this matte the copper can be recovered by suitable treatment. The residual sulphur of the charge thus serves as a means of extracting the copper and is itself removed in effecting that end; from a practical point of view, too, the production of a small quantity of matte is advantageous in that it promotes the easy running of the furnace and gives cleaner slags.

The chemical reactions, already described, by which lead is produced from its compounds under metallurgical conditions are all operative in the blast furnace, though to an extent which varies considerably according to conditions and the composition of the charge. The roasting-and-reaction process is generally quite subsidiary, for the atmosphere in the furnace is essentially a reducing one and oxidation of sulphide to sulphate, necessarily, does not take place to any great extent. 'Reaction' between sulphide and sulphate, however, is always possible in the hotter parts of the furnace, when both compounds are present in the charge.

Reduction of galena by iron, or precipitation, is at times an important reaction in the blast furnace, though it carries with it the same drawbacks as were mentioned in the section on reverberatory smelting, viz. the production of excessive amounts of matte, which demands costly treatment for the recovery of lead and copper contained in it. Formerly, metallic iron was added to the charge; now it is customary to add oxide ores of iron, roasted matte, and iron slags, *i.e.* materials reducible in the furnace to iron which is then available for reaction with lead sulphide. With the present methods of smelting, however, the importance of these ferruginous materials is based rather on their slagging properties than on their suitability for bringing about the reaction of iron-reduction.

The typical reaction of blast-furnace smelting is reduction of lead oxide by carbon (and carbon monoxide). Thus the smelting of sulphide ores of lead necessitates two very distinct operations: roasting of the ores to convert the lead into oxide, the sulphur being driven off as volatile oxides; and reduction of the roasted ores in the blast furnace. In no case is roasting complete, in the sense that all the sulphur is burnt off and all the lead left as oxide. The roasted mass always contains some unaltered sulphide of lead (the amount of which compound may be supplemented by subsequent reduction of sulphate), and lead is also present as sulphate and silicate. It should be added that arsenic, to a large extent, and some antimony, if these metals are present, are volatilised during the roasting.

ROASTING OF THE ORES.

The old method of roasting in heaps is sometimes, though rarely, used for pyritic ores poor in lead. The construction of the heaps is simple. The ground is first cleared and levelled, a bed of fine ore is laid down, and then the wood for kindling the heap. Upon the wood, the ore is piled; first the main bulk of coarse ore, over this the fines and, over all, the slimes, the whole forming a pyramidal heap which may vary very greatly in dimensions. At Port Pirie, N.S.W., the heaps are 250 feet long, 20 feet wide, and 6 feet high, the material being ore-slimes which are dried and cut into blocks. The sulphur-content is reduced from 12 to 7 p.c. by this treatment.

Roasting in Cylinder Furnaces.—There are two types of revolving cylinders, the rotation being either about a horizontal or a sloping axis. The Brückner cylinder exemplifies the first type. The dimensions of these cylinders vary from 12 by 6 feet to 26 by 8 feet, the charges being 4 and 25 tons respectively. They make one revolution in 40 minutes and are supplied either with stationary or movable fire-boxes, the latter being preferable when roasting proceeds of itself after ignition of the ore. The time taken to work off a charge varies from 3 to 24 hours, according to the nature of the materials.

The Oxland cylinder is an example of the second type. It is used at Laurium, in Greece, for roasting concentrates containing Pb, 60 p.c.; S, 20 p.c. This furnace is 42 feet 9 inches long, 3 feet 1 inch diameter inside; it makes one revolution in 4 minutes and roasts the charge down to 4 p.c. of sulphur.

Roasting in Reverberatory Furnaces. — Mechanical reverberatories such as those used in roasting copper ores find a somewhat limited application for the roasting of lead ores. Of these furnaces, some have fixed hearths and movable rabbles, *e.g.* the Wethey, Ropp, and Keller furnaces; others have revolving hearths and fixed rabbles, *e.g.* the Brunton, Heberlein, and Godfrey furnaces. It will suffice for our purpose to describe one of these briefly, and the Ropp Straight Line furnace will be selected as the one which has, perhaps, found most favour in the treatment of lead ores. Reference to the annexed diagram (Fig. 7) will help to make clear the description.

The Ropp is a rectangular furnace with 3 or 4 fireplaces disposed on one of the long sides. Four or six rabbles work on the hearth. The ploughs which stir the ore are set at an angle of 45° to the rabble arms. These are attached to a vertical rod passing through a slot 1½ inches wide which runs continuously down the middle of the hearth. An endless wire rope, driven by power, links up these arms and passes round two pulleys at the ends of the furnace. The complete revolution of the rabbles takes 3½ minutes, and as they are outside of the furnace for more than half that time, they become cooled and preserved thereby from injury. At each end of the furnace are swinging doors, through which the rabbles enter and leave the furnace. The working doors are placed at suitable intervals along the longer sides of the furnace. The ore is charged at one end of the furnace, traverses it in the direction opposite to that of the hot gases, and is discharged at the other end, remaining in the furnace 6–8 hours. The length of the hearth varies from 100–150 feet, the width from 11–14 feet, in the clear; the large furnaces put through 50–80 tons of ore in 24 hours, with a coal consumption of 13 p c., and an expenditure of 5–8 h.p. for working the rabbles.

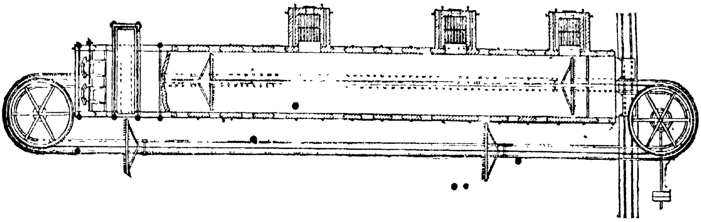

FIG. 7.—THE ROPP FURNACE.

(*From* Schnabel's 'Handbook of Metallurgy.' Macmillan & Co., Ltd.)

The use of mechanically rabbled furnaces for roasting lead ores suffers, however, from certain disadvantages. Galena is difficult to roast; it must be finely divided and the temperature must be regulated so that incipient fusion of the mineral is avoided, otherwise the fritted material becomes impervious to air and oxidation is arrested. With progressive conversion of sulphide into oxide and sulphate, the risk of fusion is lessened; at the same time, it is desirable that the temperature should be increased in order to hasten the oxidation of the unaltered sulphide. The advantage of a temperature-gradient in the furnace, coupled with the transportation of the charge as oxidation progresses, from the cooler to the hotter parts, becomes obvious. These conditions are best attained in the long-bedded, hand-worked reverberatories (*Fortschaufelungs* furnace), and these furnaces have been, and still are, extensively used for roasting lead ores.

The construction of this furnace will be understood from the accompanying figures, for the drawings of which and also for much information respecting the present practice of lead smelting, the writer is indebted to Mr. W. Maynard Hutchings.

Fig. 8 is a front elevation of the furnace, which is constructed of brickwork with a lining of fire-brick, and stayed together with iron standards and crossbars. In this is also shown the hopper *a* for charging ore, the ten working doors *b*, the door *c* for the withdrawal of the charge, and the door *d* for charging the fuel.

Fig. 9 represents a vertical section, showing the fire-grate *e*, the fire-bridge *f*, and bed of the furnace, constructed of iron plates supported by pillars of brickwork, which are cooled by circulation of air below; upon these plates are built the materials composing the bed of the furnace. *g* is the opening in the roof through which the ore from the hopper is discharged into

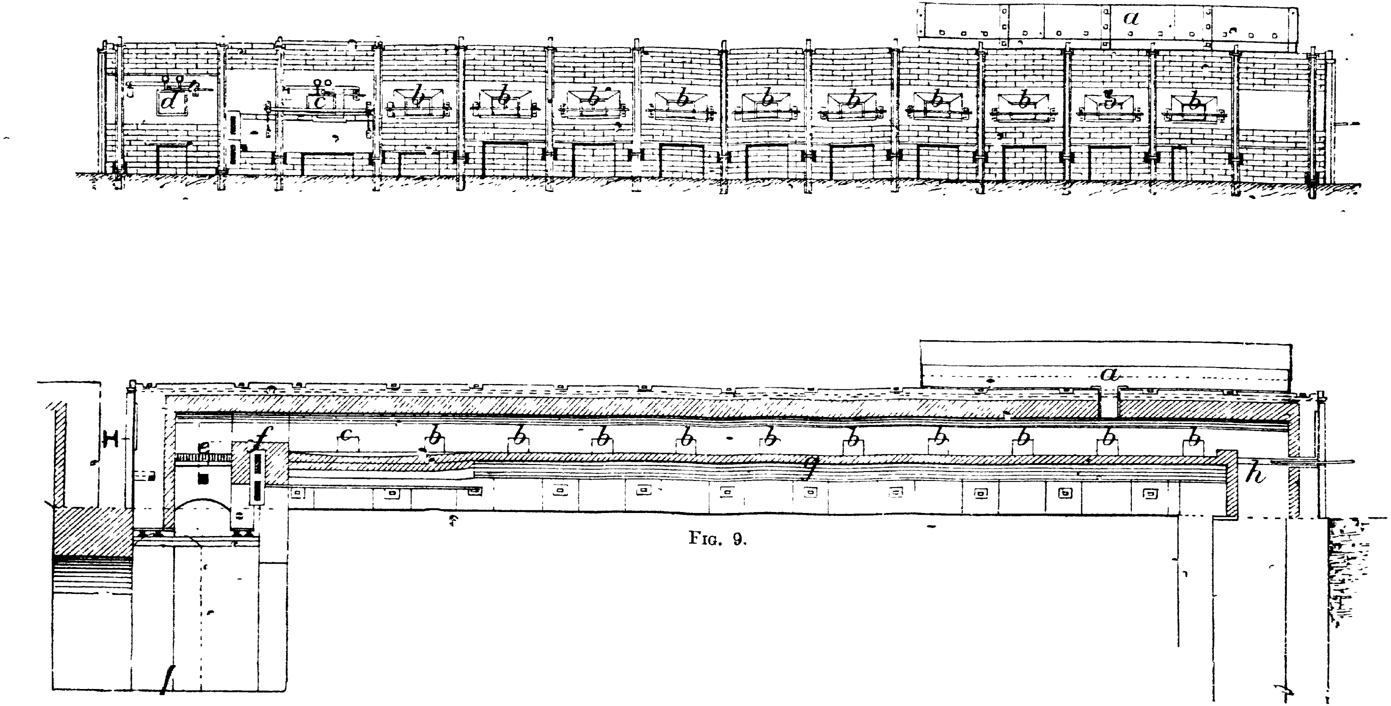

FIG. 9.

the furnace bed, *h* the flue leading to a series of condensing chambers.

Fig. 10 is a plan of the furnace, and Figs. 11 and 12 are vertical sections through CD and FG respectively.

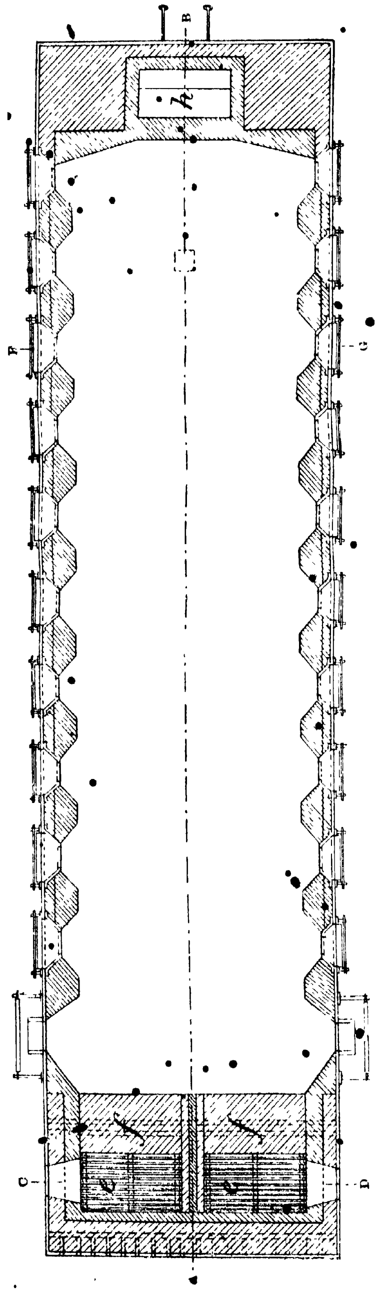

FIG 10.

The usual size of these furnaces is 60 feet by 16 feet; occasionally they are much longer—up to 80 feet—but the breadth is limited by the necessity of working the charge from each side. The bed of the furnace is sometimes divided into four hearths, each with a step of 2 inches towards the fire-bridge, and having two working doors at either side. The ore is charged on the hearth furthest removed from the fire and spread out in a layer 3–6 inches thick. The roasted ore is discharged through an opening in the hearth nearest the fire-bridge, and the ore from each hearth raked up in turn, so that it is subjected to a gradually increasing temperature as the oxidation of the sulphide proceeds. Sometimes the roasted ore is discharged as a powder, in which case it has to be briquetted before smelting; more usually it is sintered, a sump being provided near the fire-bridge (*v.* Fig. 9) in which the semi-fused mass is collected and from which it can be raked into slag pots and agglomerated by tamping. When complete fusion is required (this is not advisable when the ores are rich in silver) the furnace sometimes has a separate hearth next to the fire-bridge, smaller, and at a lower level, than the main ones, and connected with them by a vertical flue about 2 feet 6 inches high. Sand may be strewn on the fusion-hearth before the charge is raked on The effect of this is to decompose the lead sulphate, lead silicate being formed on fusion and sulphur trioxide driven off. As lead sulphate is reduced to sulphide in the blast furnace, this method of treatment lessens the matte-fall. The charge is melted in this hearth, raked into slag pots and broken up before smelting. This method of treatment, slag-roasting as it is termed, is less favoured by smelters than sinter-roasting, which leaves the material in a porous condition suitable for the blast furnace.

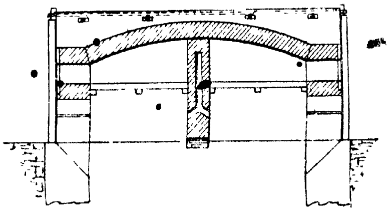

FIG. 11.

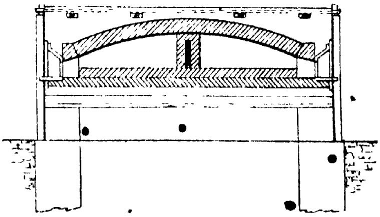

FIG 12.

Heap-roasting may be combined with cylinder- or reverberatory-roasting, and any of these with the method of blast-roasting which will now be described.

Blast- or Pot-Roasting.—In 1896 Huntington and Heberlein introduced a method of treating galena, and concentrates consisting of galena mixed with pyrites and blende; by this process the ore is rapidly desulphurised and obtained in a condition suitable for the blast furnace, and incidentally the sulphur dioxide produced may be utilised for the production of sulphuric acid. In this process the ore is mixed with 6 to 15 p.c. of lime or limestone, according to the proportion of sulphur in the ore, and roasted in a reverberatory furnace. The partially desulphurised material is transferred to a pear-shaped pot or converter, made of sheet iron, in which it is submitted to the action of a blast of air; during the blowing in the converter, energetic oxidation takes place, accompanied by other reactions, resulting in a rise of temperature sufficient to bring about agglomeration of the mass. This principle has been modified in various ways and has attained great importance, during recent years, in the practice of lead-smelting. The modifications are concerned with the materials added to the charge and with the manner in which the air is supplied. In the original process the air is blown upwards through the charge, and this arrangement is adopted in the Carmichael-Bradford and Savelsberg modifications, which are thus termed 'up-draught' processes. In the Dwight-Lloyd process the air is drawn downwards, by suction, through the charge, and the term 'down-draught' is therefore applied to this process.

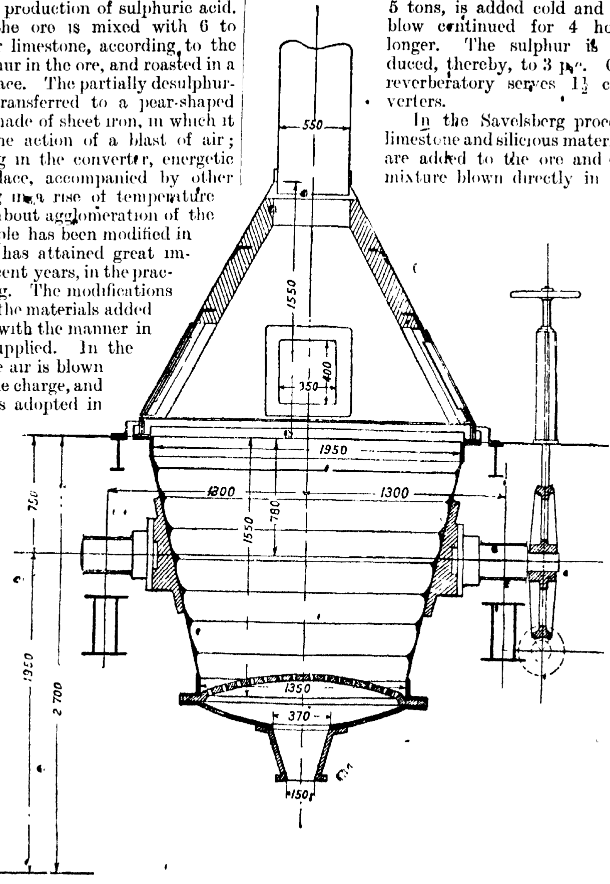

Fig. 13.

(*From* Collins' 'Metallurgy of Lead.' C. Griffin & Sons.)

The converter used in the Huntington-Heberlein process is shown in Fig. 13. The blast enters by a pipe at the bottom of the converter and the charge rests on a false bottom, consisting of an iron grate, which serves to distribute the blast. When in action, the top is covered by a hood through which the fumes escape; after the roasting is completed, the hood is removed, the converter tipped, and the agglomerated mass allowed to fall some distance in order to break it up. Such a converter takes a charge of 8 tons.

To start the operation, a small fire is lighted in the converter and some hot, partly-roasted ore added. A low-pressure blast is turned on, and then the main bulk of the ore, which may be either hot from the reverberatory roasting, or cooled and moistened with water, is added from time to time in suitable quantities, the blast pressure being increased. The method used at Braubach (Prussia) may be quoted as an example. The ores are roasted in reverberatories down to 10 p.c. of sulphur. The pots hold 11 tons. One ton of hot ore is put in first, then 5 tons of cold ore on top. After 8 hours' blow, the remainder of the charge, 5 tons, is added cold and the blow continued for 4 hours longer. The sulphur is reduced, thereby, to 3 p.c. One reverberatory serves 1½ converters.

In the Savelsberg process, limestone and siliceous materials are added to the ore and the mixture blown directly in the converter, the preliminary roasting of the charge being omitted.

In the Carmichael-Bradford process, the preliminary roasting of the ores is likewise omitted. The materials are mixed with calcined gypsum and water, and after the mixture has set it is broken up into small pieces and submitted to the pot-roasting process.

The chief shortcomings of these processes are that they are discontinuous, and the capacity of the converters is small. Only a comparatively thin layer of the ore is being oxidised at any particular moment, the main bulk remaining inert, either in an oxidised or unoxidised condition These disadvantages are avoided in the down-draught method of Dwight and Lloyd, the essence of which is that a thin layer of fine ore is exposed to the air and the process is continuous. As the roasting is quickly accomplished, the capacity of the machines is considerable.

One type of machine, in which the operation is carried out, is shown in Fig. 14. It consists of a continuous series of pallets, 42 inches wide by 24 inches long, composed of cast-iron grates with $\frac{1}{4}$ inch spaces. In the course of their revolution the pallets pass beneath the charging hopper and receive the moistened ore, which is spread about 4 inches thick; thence they pass to the fire-box where the surface of the charge is ignited by a flame pointing downwards, and then to the suction-box, where the roasting is effected by air drawn through the charge. Finally the roasted ore is discharged automatically at the end of the machine by the fall of the pallets to the lower track; the empty pallets return in course of time to the hoppers and the cycle of operations is repeated. One complete revolution is made in about 45 minutes.

For the efficient working of this process, the sulphur in the charge should not exceed 18 p.c. In the treatment of concentrates, either preliminary roasting in a reverberatory is necessary, or the concentrates must be diluted with poor ores before being roasted by the Dwight-Lloyd process. By the adoption of a double roast, either in Huntington-Heberlein and Dwight-Lloyd converters, or in a double set of the latter, it has been found possible to avoid reverberatory roasting and dilution; sulphur is reduced to 2-3 p.c., and in the subsequent smelting the yields of matte and slag are small.

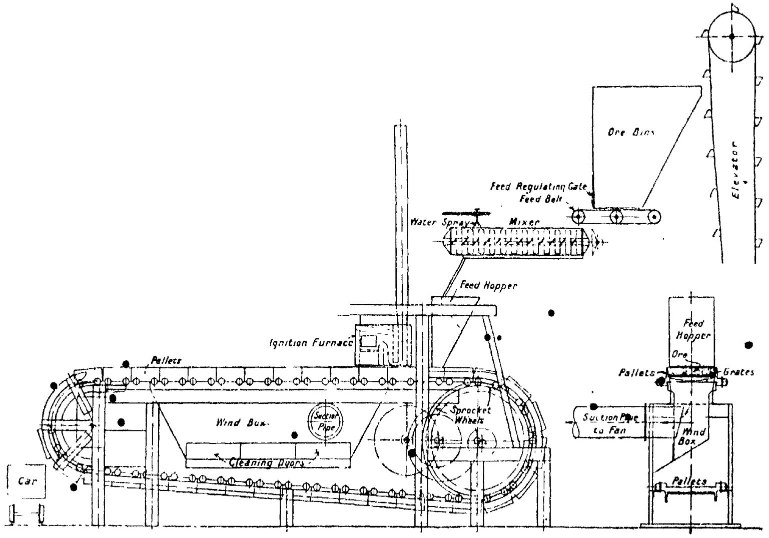

FIG. 14.

(*From* Collins' 'Metallurgy of Lead.' C. Griffin & Sons.)

The chemical reactions taking place during blast-roasting have been the subject of much speculation and discussion. The conversion of lead sulphide into lead oxide is the reaction of prime importance, and this is generally assumed to be the result of the interaction between sulphide and sulphate, as expressed in the equation:

$$PbS+3PbSO_4=4PbO+4SO_2$$

It may be noted that a similar reaction occurs when barium sulphate is heated in the electric furnace, the process being one which might be termed, by analogy, reduction-and-reaction. It is likely, however, that some oxide is formed by direct oxidation of lead sulphide. There are few actual and possible constituents of the converter charge which have escaped the suspicion of acting as catalysts in the oxidation of the lead sulphide, though it cannot be said that the claims of most of them as oxygen-carriers are well established. Most of the controversy on this subject has been centred on the function of the calcium compounds. When lime or limestone is present, there is evidence from the glowing of the charge on gently heating that reaction with galena takes place, the result being, apparently, the formation of calcium sulphide and lead oxide (carbon dioxide being liberated when limestone is used). The calcium sulphide is then rapidly oxidised to calcium sulphate, though by what agency is not apparent. The result is, however, that no matter what compound of calcium is used, the oxidation of the ore is effected, for the greater part, in presence of calcium sulphate. The facilitation of the roasting-process by means of this compound has been demonstrated (*see* W. M. Hutchings, Eng. and Min. Journ. Oct. 1905). It will be clear that, apart from the possibility of calcium sulphate acting as a catalyst, there are many possibilities of reaction among the oxides, sulphides, and sulphates of lead and calcium, especially in presence of atmospheric oxygen. That some reaction between sulphide and sulphate of lead, like that which is the basis of the roasting and reaction process, takes place is evident from the production of prills of metallic lead (*see* W. R. Ingalls, Amer. Inst Min. Eng. July, 1906).

Of the secondary reactions which occur, particular mention should be made of the formation of silicates of lime and calcium by the interaction of silica with lead oxide, lead sulphate, and calcium sulphate. In the last two cases, sulphur trioxide is evolved and the passage of this, at a high temperature, through the charge has undoubtedly a powerful oxidising action on the unaltered galena (Hutchings, *l.c.*).

The possibility of blast-roasting without the addition of calcium compounds indicates that though these may facilitate the reactions, they are not essential to the effective oxidation of galena, but that the conditions of air-feed peculiar to the converter-process are primarily responsible for the efficiency of this process. Mention should be made, too, of the mechanical effect of the added materials, whatever their nature may be, in keeping open the charge, and preventing premature agglomeration of the ore.

SMELTING THE ROASTED ORES.

There are two types of blast furnace in general use, the round or circular and the rectangular. The first is exemplified by the Pilz, the second by the Raschette furnace. An old form of the Pilz is represented in the accompanying diagram (Fig. 15). It is 25 feet high, 4 feet 11 inches in diameter at the tuyeres, gradually widening to 6 feet 7 inches at the throat, and is supplied with 8 tuyeres.

a is the hearth bottom, composed of four courses of bricks, the lowest of common brick, resting on a circular plate of from 1¼ inches thick, then three courses of fire-bricks, all encased in boiler-plate, made in segments screwed together and further strengthened by hoops of wrought iron; *b*, channels extending through the brickwork and open at both ends; these channels, of which there are two, at right angles, allow of the escape of moisture; *c c*, brickwork forming the inner and upper part of the hearth; *c′ c′*, brickwork of the boshes; *c″ c″*, brickwork forming the shaft; *d d*, the tap holes, of which there are four; *e e*, two slag lips, along which the slag flows into the slag pot *p*, consisting of a cast-iron conical vessel; *f f*, blast pipes, the horizontal portions of which can be moved to and from the tuyere holes; the vertical portions are supplied with a sliding screw by means of which they may be moved up and down; *g g g* are wrought-iron water-jackets made in sections, the construction of which is shown in detail in the accompanying illustrations. Water-jackets may also be constructed of cast iron, each segment being provided with an aperture for the tuyere and also pipes for conveying the cold water and for the outflow of the heated water; *h h*, ring of angle iron, riveted to the outer case, serving for the support of the shaft during the repairing of the lower part of the furnace; *i i*, blast main of cast iron; *k*, ring of iron supported by the four cast-iron pillars *l l*; *m*, cast-iron cylinder, flanged at the top and inserted into the mouth of the furnace, in order that the fume and waste gases may be drawn off by the pipe *n*; *o*, charging floor; *q*, outer iron casing of the furnace. The water-jackets are ⅓ of an inch in thickness, and are riveted to angle iron 2⅜ inches by ⅜ inch; *s s* are side plates overlapping by 2¾ inches top and bottom; *t*, pipes for supplying cold water; and *u*, pipe for the outflow of cold water; *v*, tuyeres, which are 2¼ inches in diameter.

The diameter of circular furnaces varies from about 36 to 60 inches, the smaller being used for powdery, the larger for lumpy ores. The number of tuyeres varies from 8 to 24, and the blast pressure from 10 to 50 mm. of mercury. These furnaces are limited in diameter by the range of penetration of the blast, which is about 36 inches. They are chiefly used in small works, and especially in Europe. All modern ones are fitted with the Arendts' or automatic syphon tap, which will be described presently, and they are usually boshed for the better utilisation of the heat and reducing gases and the more uniform descent of the charge.

The rectangular furnace is developed from the Raschette and, because of its great capacity, is the one almost universally used in America, where immense quantities of low-grade ore are available. The breadth of these furnaces is limited for the same reason as in the case of the circular furnaces, but the length can vary within wide limits. The dimensions of the smaller furnaces are about 42 by 84 inches, the larger ones 48 by 156 inches; an extreme size is 62 by 212 inches. A view of the lower part of one of the larger furnaces is shown in Fig. 16. This furnace is fitted with steel water-jackets.

Fig 17 shows a drawing of a complete modern rectangular furnace, of which the following is a brief description:

The shaft of the furnace, A, is made of brick and carried on a mantle ring, resting on four columns. In this are four charging doors, B, at the feed level. The top is enclosed by a hood closed by a damper, and the fumes are drawn off into the fume chambers and bag-house by a pipe (not shown in the figure). The height of the shaft is 16–20 feet. The zone of fusion is enclosed in water-jackets, C, from 3½–6 feet high. The use of these, and also of cold blast, prevents undue volatilisation and hinders corrosion of the hotter parts of the furnace. The blast is supplied at a pressure of about 130 mm. of mercury and enters the furnace by 14 tuyeres, D, each 4 inches in diameter, which pass through the water-jackets and are distributed along the two longer sides of the furnace. As a rule, there are no tuyeres in the end jackets. The tuyeres are fed from a blast main, E, the connections being well seen in Fig. 16. The lower part of the furnace or crucible, F, is built of fire-brick and magnesia brick, surrounded by brasque and securely held by enclosing iron walls and bed-plate. A channel 6-8 inches square leads from the crucible to the outside of furnace in the middle of one of the longer sides. This opens out into a basin and constitutes the automatic tap, G. The furnace is worked with the crucible full of molten lead, and the metal naturally stands at the same level in the basin as in the crucible. The lead may be run off in a continuous stream, or it may be ladled from the basin as required. The advantages of this method are that the unhealthy operation of tapping is avoided, complete separation of lead from matte and slag is effected, and the cooling which would result from emptying the crucible entirely is obviated. The distance of the tuyeres above the level of the lead bath is about 12 inches, and is so

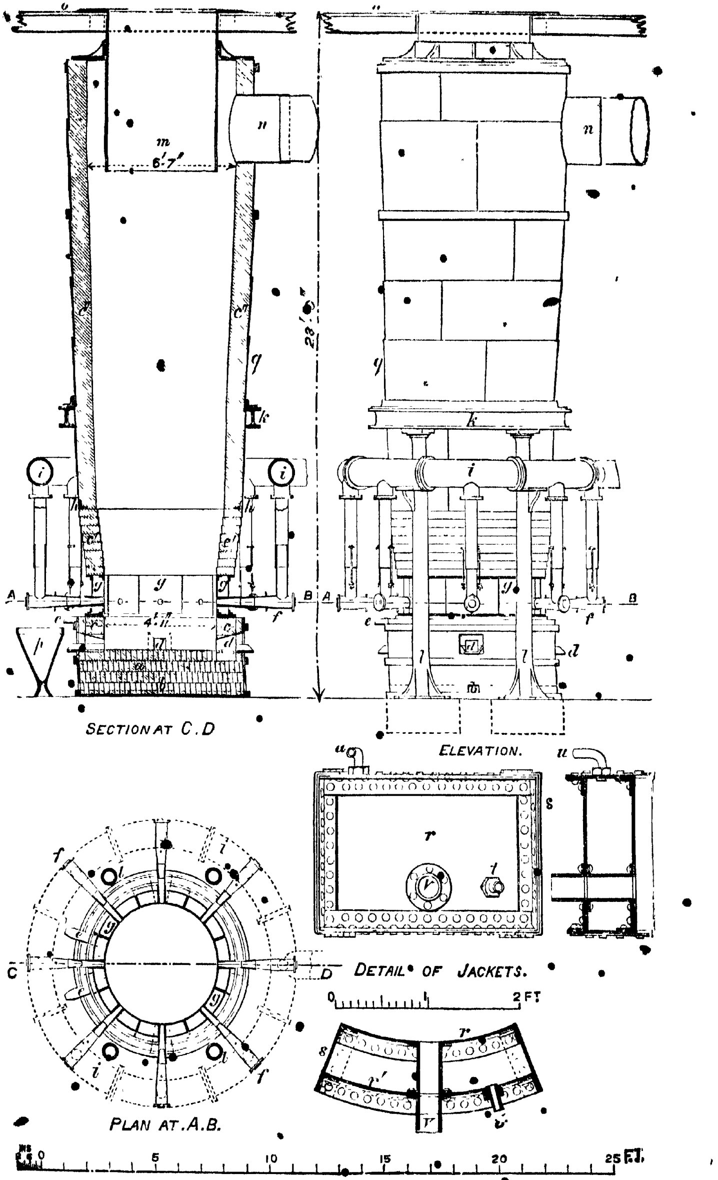

Fig. 15.

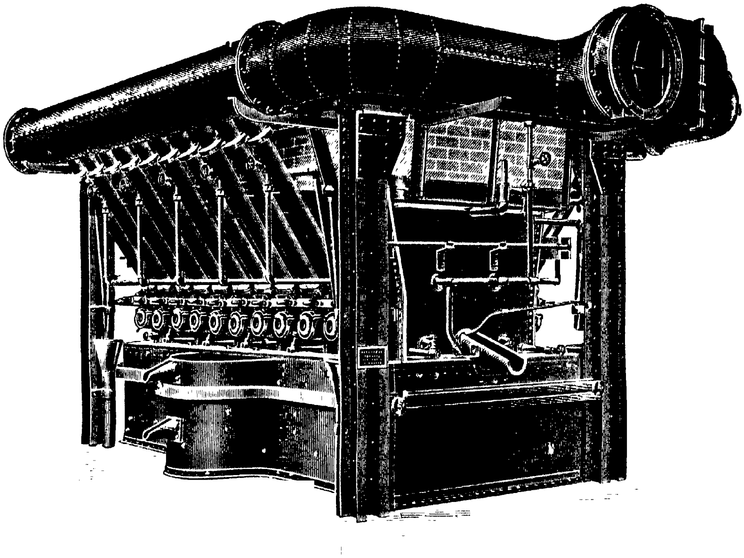

FIG 16.

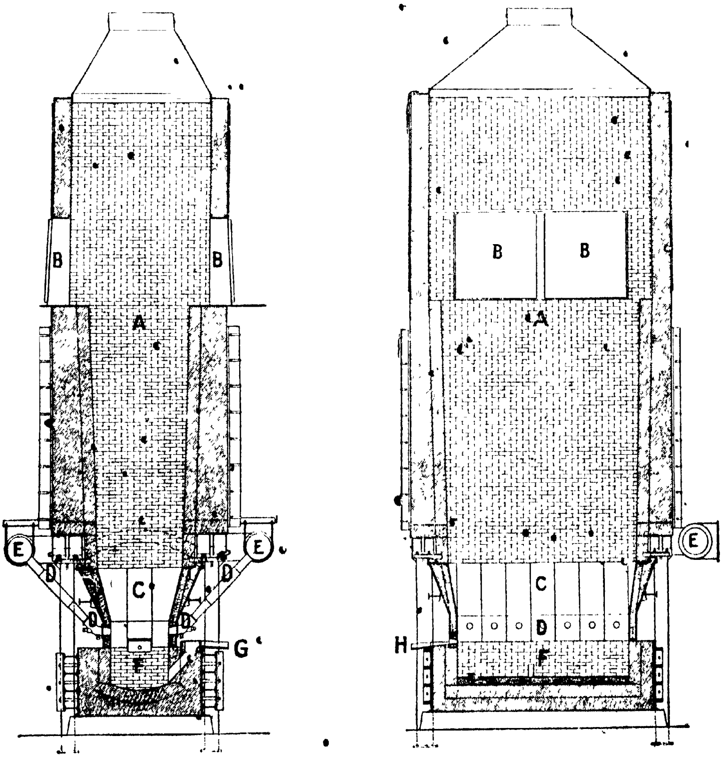

FIG. 17.

arranged that the heat is sufficient to keep the lead molten. Between the lead level and the tuyeres is a slag tap, H, from which slag and matte are continuously discharged. They are collected in settlers or forehearths, sometimes heated by a fire, and the matte tapped off from the slag. Such a furnace will put through 150–250 tons in 24 hours, with a coke consumption of 12 p c. of the charge.

The charge for blast-furnace smelting consists in general of ores and mattes, roasted by the methods already described; earthy and silicious materials either derived from the ores or added to produce the desired slag; slags from previous operations, in amount up to 20 p.c., which are added partly to recover values present in them, and partly to facilitate the furnace-running; and coke, the usual fuel and reducing agent. Sulphide ores rich in silver are generally added direct to the blast-furnace charges, in order to obviate the loss of silver which would occur during roasting. The lead-content of the charge varies considerably; 10–12 p.c. is usually regarded as a minimum consistent with the effective action of the lead as a solvent or vehicle for the silver; 50 p.c. of lead is not uncommon, and the average may be put roughly as 20 p.c.

Great care has to be exercised in the selection of materials to produce the slag. Barren fluxes are avoided if possible, silicious silver ores and iron ores from the gossans, which usually contain some lead and precious metals, being utilised where available. The objects aimed at are to produce a monosilicate, mobile when molten, and having a sp.gr. of 3·5. Analyses of slags of proved merit are given in the following table :—

	(Fe,Mn)O	(Ca,Mg)O	SiO_2
1.	50	12	28
2.	40	20	30
3.	33	24	33

No. 1 is the Freiberg type and is especially valuable for charges rich in zinc. Slags rich in zinc should be highly ferruginous and correspondingly poor in lime. The amount of zinc should not exceed 15 p.c. (reckoned as oxide). According to Hutchings (Eng. and Min. Journ. Oct. 1903), zinc is present in slags in the form of silicate (willemite), zinciferous magnetite, and zinc spinels. Alumina in slags should be kept as low as possible. Slags, to be 'clean,' should carry less than 1 p.c. of lead and 0·0015 p.c. of silver.

An outline of the chemical reactions which take place in the blast furnace, in so far as these are responsible for the production of most of the lead, has already been given (*v.* p. 50). This may be amplified by a brief consideration of the part which the silicates play in the process. Silicates of lead, iron, and calcium may be already present in the materials charged. In any case, the decomposition of limestone and the reduction of ferric to ferrous oxide, by carbon monoxide, furnish bases which unite with silica in the zone of fusion. Lead silicate may also be formed by reaction of lead oxide and silica. Complete reduction of oxide of iron by carbon yields the metal. Lead silicate is reduced by metallic iron, but it is not decomposed by lime; lime, however, displaces ferrous oxide from ferrous silicate, and as the ferrous oxide is in turn reduced to iron, this becomes available for the decomposition of lead silicate (and lead sulphide). The net result of these reactions is the production of metallic lead and a slag free from lead silicate.

Other metals present in the charge are also reduced and pass to some extent into the lead, and it is, of course, all-important that the precious metals should be very completely dissolved in that medium. Copper is largely recovered as sulphide, Cu_2S, in the matte, though some is invariably taken up in the metallic form by the lead. Arsenic is partly volatilised and partly combines with iron to form a speiss which carries some copper, lead, and silver, and practically all the nickel and cobalt present.

The products of the blast furnace are lead, matte, speiss, slag, and flue dust. The *lead*, known as work-lead or base-bullion, is almost always hard and impure, and is submitted to refining and desilverising processes, which are described later. The *matte* separates from the slag in the settler or forehearth. Its sp.gr. is 5–6, and should be at least one unit greater than the slag, otherwise complete separation is difficult to attain. Mattes usually contain 10–20 p.c. of lead, along with some copper, the composition varying within wide limits, as may be seen from the following analyses :—

COMPOSITION OF MATTES.

	Oker	Przibram	Laurium	Dapto
Iron . .	30·5	41·3	50·8	46·6
Lead . .	5·1	11·2	7·7	15·4
Copper .	16·8	1·5	1·8	3·9
Zinc . .	16·3	11·5	7·6	6·4
Sulphur .	16·4	22·2	21·8	25·0

Mattes always carry some silver and gold, but silver is relatively more soluble in them than gold. They are roasted and added to blast-furnace charges, whereby the iron becomes available for slagging and reduction purposes, and a new matte, enriched in copper, is formed. When the copper-content rises to 10 p.c., the mattes are roasted down to 3–4 p.c. of sulphur and then smelted with liquation-residues and silicious copper ores. After enrichment to 30–40 p.c. of copper, they are usually sold to the copper smelters and treated for copper by the converter, or some other, process.

Speiss is formed in blast-furnace practice only when the charges are rich in arsenic or antimony and iron. It is essentially an arsenide (and antimonide) of iron, carrying some silver, a relatively large amount of gold, some lead and copper, and practically all the nickel and cobalt. Except in isolated cases, the last two metals are of no importance in blast-furnace products; a speiss rarely contains 5 p.c. of them. Some Freiberg speisses, however, have more than double this amount.

The composition of speiss is illustrated by the following table of analyses (values, per cent.) :—

COMPOSITION OF SPEISSES.

	Przibram	Laurium	Meadville	Freiberg
Silver .	0·037	0·011	0·008	0·077
Iron . .	61·3	63·8	60·6	17·8
Arsenic .	18·5	20·7	31·5	23·4
Antimony .	2·4	—	—	6·5
Lead .	1·7	0·5	1·5	11·2
Copper .	1·9	0·6	0·4	24·2
Nickel and cobalt	2·2	—	0·1	11·3
Sulphur .	9·6	4·6	5·8	3·5

Speiss is desilverised by smelting in the blast furnace; copper passes into the matte and nickel and cobalt are concentrated in the new speiss. Thus, a raw speiss containing 6 p.c. of nickel and cobalt and 0·16 p.c. of silver yielded on smelting a new speiss containing 16 p.c. of nickel and cobalt and only 0·05 p.c. of silver. Rich speisses may be roasted with pyrites, when the arsenic is volatilised as sulphide, and the residues smelted with silicious additions in the blast furnace.

Slags have already been considered with respect to their composition and fitness for the smooth running of furnace work. The clean separation of slag from matte (and speiss) is of great importance, and depends largely on their relative fluidities and specific gravities. Matte is dissolved to some extent by slag, acidic slags dissolving less than basic, and calcareous less than ferruginous slags.

Flue dust.—The methods for the collection and treatment of this will be described later. The waste gases from the blast furnace contain 5–10 p.c. of carbon monoxide, and 15–20 p.c. of carbon dioxide, the remainder being chiefly nitrogen.

The loss of lead in the blast furnace is variable, 7 p.c. on the dry assay being considered satisfactory. The loss of silver is very small by this method, whereas in the roasting-and-reaction process the average loss is about 1·5 p.c.

The basis of the modern American and Australian practice of lead-smelting is blast roasting of ores, either by the Huntington-Heberlein or Dwight-Lloyd methods, either singly or combined. This is sometimes preceded by roasting in cylinders or reverberatories and is followed by smelting of the roasted ore, with the addition of suitable fluxes, in rectangular, water-jacketed furnaces of large capacity.

In order to illustrate the principles and methods described above, some examples of blast-furnace smelting will now be considered.

EXAMPLES OF SMELTING.

Smelting at Clausthal.—As an example of the practice of the 'iron precipitation' process, the treatment adopted at Clausthal may be cited.

The ores are dressed and supplied to the smelter in the form of *schlieg*, having the average composition :—

Lead	50 7	to 73 6 p.c.[1]
Silver	0·555	,, 0·185 ,,
Copper	0·02	,, 0·6 ,,
Zinc	0·3	,, 4·1 ,,
Antimony	0·02	,, 0·3 ,,
Iron	0·4	,, 3·7 ,,
Sulphur	8·5	,, 14·2 ,,
Alumina	0·07	,, 1·5 ,,
Lime	0·2	,, 1·4 ,,
Insoluble residue	5·9	,, 32·4 ,,

The furnaces are circular, 23 feet high, 3 feet in diameter at the tuyeres, and 5 feet at the throat; they are furnished with 4 tuyeres.

The charge consist of *schlieg*, lime, roasted lead matte, slags obtained in smelting ore, and slags obtained from the smelting of matte, together with Oker slags, the residue left in the wet extraction of copper ores. These two last-named materials supply the iron required for the reduction of the lead ore, the former as silicate, and the latter as sesquioxide.

The following is an example of the composition of the charge :—

	Cwt.
Ore	100·00
Lead fume	1·01
Lead scrapings from the smelting house	0·63
Roasted lead matte	47·51
Schlieg scrapings from the charging floors	1·21
Oker slags	60·00
Slags from the same process	3·70
Matte slags	42·00
Slags from schlieg smelting	54 00
	310·06

The products obtained are work-lead, lead matte, and a slag containing some lead.

Two analyses of the work-lead are given in the following table : —

Lead	98·8378	98·9648
Copper	0·1862	0·2838
Antimony	0·5743	0·7685
Arsenic	0·0009	0·0074
Bismuth	0·0039	0 0082
Iron	0·0035	0·0028
Zinc	0·0025	0·0028
Nickel	0·0023	0 0028
Cobalt	0·0006	0 0003
Cadmium	trace	trace
	99·6130	100·0414

The lead is refined at Lautenthal, or, if it contains sufficient silver, is desilverised by Parkes' process. The average silver content is 0·14 p.c.

The following analysis gives the composition of the lead matte:

Sulphur	26·877
Iron	53 112
Lead	10·655
Copper	4·620
Silver	0·030
Antimony	0·267
Arsenic	—
Zinc	2 110
Manganese	0·385
Cobalt and nickel	0·306
Lime	0·383
Magnesia	0·054
Silica	0·510
	99·309

The matte is roasted in heaps and then smelted in the ore furnace. When the copper content exceeds 6–7 p.c., the roasted matte is smelted in a low blast furnace with slags from ore smelting and coke. The work-lead from this operation contains 0·4 to 1·5 p.c. of silver; the matte is again roasted and smelted until the copper content rises to 20 p.c., when it is treated for the extraction of copper.

Smelting at Binsfeld.—The ores containing 70 p.c. of lead are mixed with limestone and sand and roasted in the Dwight-Lloyd machine. The roasted material contains 58 p.c. of lead. 1000 parts of this are mixed with 180 of ferruginous slag, 50 of spathic iron ore, 400 of slags from the same operation, and 100 of various lead-bearing materials. This is then smelted in rectangular blast-furnaces, 40 by 148 inches at the tuyeres. Each furnace has 19 tuyeres and smelts 250 tons of the charge in 24 hours, yielding 70–80 tons of lead. The slags carry 2 p.c. of lead.

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[1] Karl, Grundriss der Metallhuttenkunde, p. 60.

Smelting at Trail (British Columbia).—The chief ores are sulphide, which are mixed with lead matte and limestone so as to have the following composition:—

Lead	40–44 p.c.
Ferric oxide	10–13 „
Limestone	7–10 „
Silica	8–11 „
Sulphur	14–17 „

This mixture is roasted in revolving hearths so as to bring the sulphur down to 8–9 p.c. It is then further desulphurised and sintered by blast-roasting in Huntington-Heberlein pots, of which there are 24, each 8 feet 8 inches in diameter. The charge for the blast-furnace is made up of 85 parts of the sintered material, 2·5 of oxidised lead ores and silicious gold and silver ores, and 12·5 of coke, the average lead content being 40 p.c. and the sulphur below 4 p.c. This is smelted in rectangular blast furnaces 45 by 160 inches at the tuyeres, the blast pressure being 32 ozs. and the height of the column above the tuyeres 17½ feet. The output of work-lead per day from each furnace is 75 tons, and the composition is shown in the following table:—

Lead	98·5 p.c.
Copper	0·22 „
Zinc	0·098 „
Bismuth	0·013 „
Antimony	0·32 „
Arsenic	0 28 „

The base bullion carries 100 ozs. of silver and 0·1 oz. of gold per ton. It is cast into anode plates and refined electrolytically by the Betts' process.

The slags carry 1 p.c of lead and 0·4 oz. silver per ton, and have the following percentage composition: $(Fe,Mn)O = 24–30$; $(Ca,Mg)O = 18–20$; $ZnO = 7–12$; $Al_2O_3 = 8–16$; $SiO_2 = 31–33$.

Smelting at Freiberg.—The ores are partly native and partly foreign, the latter being chiefly Canadian. They are classified according to their composition, and their treatment depends upon this. Ores containing over 25 p.c. of sulphur are roasted at the sulphuric acid works, the lump ore in kilns and muffles down to 3–6 p.c. of sulphur, the fines in *Schüttöfen* down to 8 p.c. of sulphur. Galena, containing over 30 p.c. of lead, and leady ores with 10–30 p.c. lead are mixed with roasted fines, and other materials, and roasted either in long-bedded calciners or Huntington and Heberlein pots.

The reverberatories are 54 feet 6 inches long, and 14 feet wide; they put through 12 tons in 24 hours, the separate charges being 1·5 tons. The charges consist of 2·1 parts of galena and leady ores, 1·2 of dry silicious ores (containing less than 10 p.c each of lead and sulphur), and 2 parts of roasted fines, and they are divided into rich ores, carrying 0·5–0·7 p.c. of silver, and poor ores, carrying 0·1–0·3 p.c. of silver. The composition before and after roasting is given in the following table—

		Lead (p.c.)	Zinc (p c.)	Copper (p.c.)	Sulphur (p c)	Silica (p.c.)	Silver (p.c)
Rich ores	Before roasting	24	—	0 5	12·5	22	0 48
	After roasting	26	—	1·0	4·3	24	0 64
Poor ores	Before roasting	30	7	—	8·4	22	0 09
	After roasting	33	11	—	2·6	23	0 11

The converters for blast roasting hold 2·3 tons. Roasted fines are added to the ores instead of limestone, and the charge for pre-roasting is made up of 2·4 parts of galena, 0·9 of dry ores, and 1·5 of roasted fines, and averages 36 p.c. of lead and 14 p.c. of sulphur. This is roasted in rotating furnaces, the sulphur being reduced thereby to 10 p.c and the roasted product mixed with 50 p.c. of the ore-mixture and again roasted in Huntington and Heberlein converters; in this way the sulphur is brought down to 3 p.c.

For smelting, circular furnaces of the Pilz type are used. The largest of these are 36 feet high, 6 feet 6 inches diameter at the tuyeres, and 8 feet at the throat; there are 20 tuyeres, and the blast pressure is 10–15 mm. of mercury. The charge consists of the roasted ore mixed with about two-thirds of its weight of slag from a previous operation, 2 p.c. of burnt pyrites, and small amounts of dry ores. The consumption of fuel (coke) is about 15 p.c. of the charge. The work-lead contains 0·5–2 p.c. of silver; the matte-fall is about 10 p.c., and the matte contains 20–25 p.c. lead, 6–10 p c. of copper, and 0·1–0·25 p.c. of silver; the slags carry 4–6 p.c. of lead and 0·015 p.c. of silver. It is characteristic of Freiberg practice that no attempt is made to produce clean slags. They are re-smelted with roasted matte and leady additions, the latter being added in such quantity as to yield sufficient lead to keep the new matte poor in precious metals. After one or two slag-smeltings, a clean slag is produced which can be thrown away. A typical analysis of such a slag shows: lead, 1–2; silver, 0·001; copper, 0·3; zinc, 9–12; ferrous oxide, 50; and silica, 30 p.c.

Smelting at Broken Hill.—The concentrates treated by the Associated Smelters' Proprietary Co. contain 60 p.c. of lead, 15 p.c. of sulphur, and 20–25 ozs per ton of silver. Two processes for roasting the concentrates are used.

1. The ore is mixed with ground limestone and ironstone, moistened and charged on to the Dwight-Lloyd machine. Thence it is conveyed to the rolls, ground and moistened and roasted again in a similar manner.

2. The ore-mixture, as above, is roasted in a Ropp furnace, 156 feet long and 14 feet wide. The roasted material is charged hot into Huntington and Heberlein converters of 10 tons capacity, and air blown through at 1½ lbs. pressure. The sintered mass is tipped and broken up and is ready for smelting. The output of 3 Ropp roasters, 20 converters, and 9 Dwight-Lloyd machines is 500–550 tons a day.

The roasted ore is smelted in rectangular blast furnaces 17 feet long, 4 feet 6 inches wide, and 25 feet high over all. Three of these are used, and they are capable of putting through 1200 tons of total charge a day. The charge consists of roasted and sintered ore, ironstone, limestone, slags from a former smelting, and coke. The daily output of base bullion is 400 tons, containing 40–50 ozs. per ton of silver, and, in addition, copper (0·5 p.c.), antimony, and arsenic. The slags are clean and amount to 750 tons a day; 20–25 tons of fume are condensed every week by bag-filtration, and this is collected and re-smelted to recover lead.

Though somewhat premature, an outline of the method of treating the base bullion will be given here for the sake of completeness. The base bullion is run into a drossing furnace and the copper removed. The dross amounts to 5 p.c. of the bullion and contains 10 p.c. of copper. The bullion is then tapped into an improving furnace of 65 tons' capacity and drossed for 12 hours. The antimonial slag (5–7 p.c. antimony) thus produced is smelted in a reverberatory furnace and yields a richer slag containing 12–13 p.c. of antimony; this is then smelted in a blast furnace for antimonial lead.

The purified bullion is submitted to Parkes' process. The first zincing extracts the gold, the second yields a crust containing 1500–2000 ozs. of silver per ton, and the third reduces the silver in the lead to 0·4 oz. per ton. The desilverised lead, containing 0·5 p.c. of zinc, is refined in a softening furnace for 12 hours, and yields market lead of the composition: lead, 99·9917; silver, 0·0012; copper, 0·0001; zinc, 0·001; antimony, 0 006 p.c.

The first zinc crust is melted in a reverberatory furnace with litharge derived from the cupellation process. Zinc is converted into oxide which forms a slag with the litharge; this is removed and smelted in the blast furnace to recover lead and silver. The lead is tapped from the reverberatory into a desilverising pot and again treated with zinc. This yields a crust enriched in gold. The alloy is distilled in graphite crucibles to remove the zinc and the residual gold-silver-lead alloy cupelled for doré bars which contain 2·5 p.c. of gold. The gold is parted by sulphuric acid and the silver sulphate reduced to metal or a cupel with fine coal, the metal being 993 fine.

The second crust is distilled and yields zinc, which is used again in the process, and distillery bars containing 2500 ozs. per ton of silver. These are cupelled for silver.

The third crust being poor in silver is used for zincing fresh base bullion (The Metal Industry, May 11, 1917).

SOFTENING OF HARD LEAD.

The lead obtained by smelting contains variable quantities of the precious metals. Leads from Missouri and Wisconsin, for example, are almost free from them, whereas the silver and gold in some bullion-leads is worth more than the lead which contains them. In addition to the precious metals, work-lead contains a number of base metals, most of which make the lead hard, unfit it for commercial purposes, and render the profitable extraction of silver an impossibility. The following analyses of work-lead illustrate the nature and range of the chief impurities:—

	Per cent.						Ozs per ton	
Origin	Pb	Cu	Sb	As	Bi	S	Ag	Au
English (Weardale) . . .	99·87	0·015	0·05	0·01	0 001	0·015	7	—
German (Freiberg) . . .	96·67	0·94	0 82	0·28	0 066	0·20	186	—
Spanish (Magarron) . . .	99·20	0·22	0·20	0 15	0·004	0·11	9	0·06
,, (Orcellitana) . . .	98·92	0·15	0·46	0·21	0·005	0 10	45	—
Greek (Laurium) . . .	98·27	0·75	0·55	0·10	0 010	0·08	45	0·07
Turkish (Balia Karaidini) . .	98·36	0·35	0·50	0 23	0·058	0 22	62	0·17
American (Tombstone, Arizona) .	98·50	0·22	0·32	0·28	0·013	—	200	0·10
Mexican (Torreon) . . .	95·40	0·08	1·80	1·30	0·050	0·35	300	1·50
,, (Magapil) . . .	95·72	0·09	2·50	0·90	0·030	0·32	105	0·42

There are also, on occasion, small quantities of tin, zinc, iron, nickel, and cobalt present in work-lead. Almost all of these impurities have a deleterious effect on the desilverisation process, arsenic being one of the worst in that respect, and their removal is consequently an operation of great importance. Many of them are more easily oxidised than lead, and can thus be eliminated by oxidation of the molten metal, the oxides forming a dross on the surface. Bismuth and copper are not so easily oxidised as lead. Copper, however, forms an alloy of fairly high melting-point, and can thus be removed by liquation. The elimination of bismuth is a very difficult matter; fortunately, its effect on the properties of lead is not very harmful for most purposes when present in moderate amounts. In the Pattinson process (*q.v.*) it is retained in the rich alloy and passes eventually into the litharge when the rich alloy is cupelled; it can be completely removed only by the electrolytic method of refining. In general, then, the purification of work-lead is brought about by drossing the oxidisable impurities, a process known as 'improving' or 'softening.' When the work-lead contains much copper, drossing is preceded by liquation.

Liquation is carried out at a low temperature on a hearth with sloping bottom, the lead draining away into kettles, leaving the liquation-residues rich in copper. In Freiberg, the furnaces are 5 feet 8 inches by 5 feet 6 inches; the liquation residues contain all the sulphur, 96 p.c. of the nickel and cobalt, 93 p.c. of the copper, and 25 p.c. of the arsenic which were present in the base bullion. The analysis of these residues show: lead, 62·4 p.c.; copper, 17·97; arsenic, 2 32; antimony, 0·98; tin, 0·04; nickel and cobalt, 1·09. They are treated by smelting either in small cupolas with low-grade matte, or in blast furnaces with galena, the copper being recovered in the matte.

The *improving* or *softening* is effected in a reverberatory furnace. A simple type, which was at one time the standard pattern, consists of a cast-iron pan which forms the lead bath.

It is about 2 inches in thickness, 10 feet long, 5 feet 6 inches wide, and 10 inches in depth. All the angles of the casting are carefully rounded to prevent breakage by expansion or contraction, and the softened lead is drawn off by a hole bored in the bottom, near the outer edge, which is stopped by a well-fitting iron plug held in its place by a weighted lever.

This type of furnace is usually made to hold from 8 to 12 tons of molten lead. The fireplace is about 20 inches wide, and has a length equal to the width of the cast-iron pan, from which it is separated by a bridge 2 feet wide. The height of the furnace above the pan at the bridge end is 16 inches, and at the other end 8 inches.

The charge is introduced either in the form of pigs or is first melted in an iron pot set in brickwork at the side of the furnace, and subsequently ladled into a sheet-iron gutter, by which it is conveyed to the furnace. This kind of furnace is easy to erect, but is too small for present-day conditions where large throughput is required. Modern furnaces are much larger, and have the lead bath built of brick usually set in a wrought-iron pan. They are supported on rails and held up by buckstays. The bottom of the furnace is built of a layer of brasque, and the hearth is rectangular; the size varies according to requirements and the sides are sometimes water-jacketed; the hearth slopes to the tap-hole, which is rammed with clay or furnished with a tapping plug. There are usually two working doors on either side of the furnace through which the lead is charged, and through which the scums are withdrawn. The size of the fire-grate varies considerably. Many smelters prefer small ones, which, though lengthening the period of drossing, reduce the losses by volatilisation. The capacity of these furnaces is 50 to 300 tons of lead.

In the softening process, the molten lead is submitted to the action of heated air, whereby the easily oxidisable impurities are converted into oxides, which, floating on the surface of the bath, are removed by a perforated skimmer; in this way a fresh surface is constantly exposed to oxidation. The progress of the operation is judged by taking a sample in a ladle and casting it in an iron mould; when the drossing is complete the surface presents a peculiar flaky crystalline appearance. The improved or softened lead is then tapped into an iron pot, from which it is ladled into the pig moulds, or is run from the furnace by a movable iron gutter into a series of pig moulds placed in readiness in front of the furnace. It is then ready for delivery to the desilverising plant.

When the work-lead contains tin, this is the first metal to be oxidised, and the oxide separates as a powder. This is followed by the arsenic and then the antimony dross, each of which is liquid; the metals are present as arsenate and antimonate of lead. These stages are, however, not clearly defined, but merge into one another. The complete removal of these impurities is facilitated by the addition of litharge to the bath, and becomes apparent by the change in appearance from the dark oily dross of lead antimonate to the yellow scum of litharge.

The course of the drossing is illustrated by the following partial analyses of Freiberg drosses:—

	First tin dross (powder)	Second tin dross (liquid)	Arsenic dross	Antimony dross
SnO_2 .	14·7	12·2	0·6	0·3
As_2O_5 .	0·9	11·2	16·2	4·0
Sb_2O_5 .	12·5	18·6	8·5	32·2

The duration of the process at Freiberg is 2–14 days, and the yield of refined lead 75–85 p.c.

Drosses from the improving furnace are melted in a reverberatory furnace with a little coal, whereby some lead is liberated and this desilverises the dross; the residue is smelted in blast furnaces and yields an impure antimonial lead. Much of the arsenic is volatilised in the blast furnace.

DESILVERISATION OF SOFT BULLION LEAD.

The methods used in the extraction of the silver from soft or improved lead vary according to the silver-content of the lead. Low-grade leads are submitted to a concentration-process and the rich alloy thus obtained is cupelled. The concentration is effected by the Pattinson process, or some modification of it. High-grade leads are cupelled; if fairly rich in silver, they are melted, stirred with zinc, and the alloy of zinc, lead, and silver which separates on cooling is worked for silver. This is the Parkes' process.

The concentration of silver in poor silver-bearing lead is founded on an observation made by Hugh Lee Pattinson, of Newcastle-upon-Tyne, that the crystals which first separate from a molten alloy of silver and lead are poorer in silver than the residual alloy. This discovery was made the basis of a patent by Pattinson, for 'An improved method of separating silver from lead,' the date of the patent being October 28, 1833, and at the meeting of the British Association held at Newcastle-upon-Tyne in 1838 the process was described by the originator.

The behaviour of a molten silver-lead alloy on cooling is similar to that of a salt solution. The freezing point is lowered proportionately to the amount of silver dissolved, pure solvent crystallises out and the mother-liquors become enriched in the solute with the progress of crystallisation, until finally a stage is reached when the residual liquor freezes as a whole at a constant temperature. This is the eutectic point. The alloy then has the lowest melting point and further concentration of any constituent by the process of crystallisation is impossible since the composition of the eutectic liquid and the crystals derived from it is the same.

The melting point of pure lead is 327° C.; the eutectic mixture of lead and silver melts at 303°C. and contains 2·5 p.c. of silver (about 900 ozs. per ton). In practice, this limit of concentration is never reached, the enrichment not exceeding 1·75 p.c. of silver, *i.e.* 650 ozs. per ton. Further, it is impossible to separate completely the crystals of pure lead from the freezing alloy, since they always carry with them mechanically some of the silver-bearing mother-liquors. To obtain, therefore, effective concentration of silver it is necessary to repeat the operations several times, so that the process becomes, in fact, one of fractional crystallisation.

These considerations naturally apply only to pure silver-lead alloys. The presence of foreign metals disturbs the crystallisation and concentration processes in various ways.

Copper, arsenic, and antimony have the curious effect of making the crystals of lead small, so that they are difficult to drain and thus carry silver with the retained mother liquor. Zinc, if present, acts as in the Parkes' process, carrying the silver into the first fractions and thus rendering the process inoperative. Bismuth and nickel remain almost entirely (copper to some extent) in the mother-liquors and so pass on to the cupellation process with the rich alloy.

Pattinsonising, Pattinsonage, Pattinsoniren. The operation is conducted in large cast-iron hemispherical pans, capable of holding 6-10 tons of molten lead. The small 6-ton pots are now rarely used, and in some establishments pots capable of holding 18 tons of lead are employed, the larger size requiring the use of cranes in working the ladles. A series of nine to twelve of these pots is placed side by side in a line and resting on brickwork supports. Each pot is provided with a separate fireplace, the heated gases from which are conducted round the pan by a circular flue and thence pass into a flue running the whole length of the pots by which the gases are conveyed to the chimney. In addition to the large pots, there are sometimes smaller pots placed at the side between the larger pots, and heated by a separate fire; these serve to hold some melted lead for the purpose of heating and cleaning the ladles. Along both sides of the erection in which the pots are built is a platform on which the workmen stand. The pot at one end of the series is smaller than the others, being about two-thirds the size. This is called the *market pot*; the poor lead passes to this pot and is run thence into the pig moulds. The other apparatus used in this process consists of perforated ladles made of iron ½ inch in thickness; when worked by hand the ladle is 16 inches in diameter and 5 inches deep, the holes being ½ inch in diameter, whilst when cranes are used the ladle measures 20 inches in diameter, 6 inches in depth, and the holes ¾ of an inch. The handle of the ladle is 9 feet 6 inches long, and ½ an inch in thickness. In addition to the ladle, a chisel-pointed bar or *slice* is used in stirring the lead.

Fig. 18 shows the arrangement and mode of setting a range of pots.

The method of working will be best understood by supposing the lead to be treated contains some 20 oz. of silver to the ton; the metal in the form of pigs is charged into one of the pots about midway between the *market pot* and the *rich pot*, the fire is set on and the lead melted: on melting the surface of the metal is covered with a layer of dross, which is carefully removed by a ladle and the fire then withdrawn. Water is sprinkled on the surface of the molten bath to promote cooling, and as the metal cools a cake is formed on the surface, which is detached and broken up by means of the slice, and the pieces stirred into the liquid. As the cooling proceeds the mass is kept continually stirred, and after a time crystals begin to separate at the bottom of the pot. These are removed by means of the large perforated ladle,

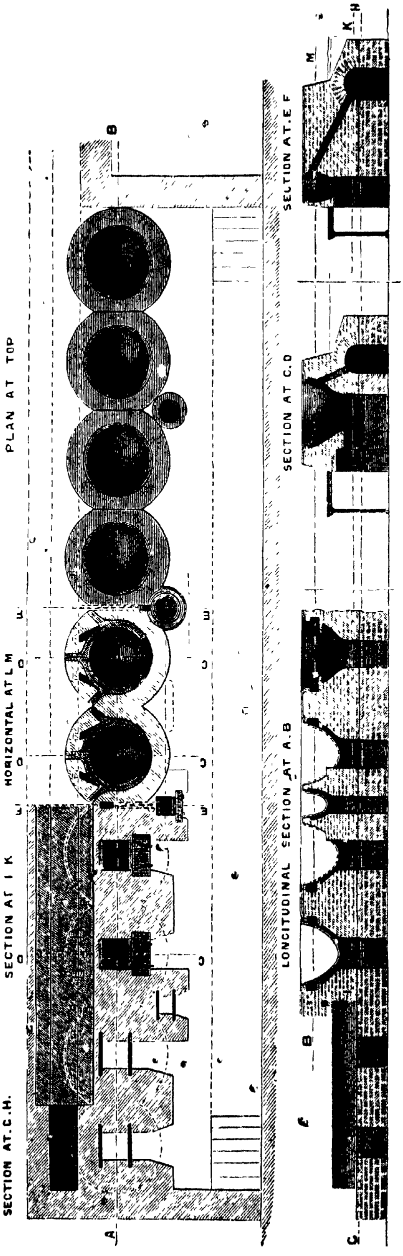

Fig. 18.

which is plunged into the liquid and then gradually raised, the side of the pot serving as a ulcrum; the ladle is raised until it is completely out of the bath and is brought into a tilted position, and the crystals allowed to drain. When drained the contents of the ladle are ransferred to the next pot on the left, supposing he market pot to be at the left extremity of the ange. This operation is repeated until two-hirds of the original charge has been transferred. The remaining third, which represents the enriched alloy, is transferred to the next pot on the right—*i.e.* toward the *rich pot.* The rich bottoms, as they are called, contain about 40 oz. of silver to the ton, and any lead that may be on hand having a similar silver content is added to the enriched bottoms. The poorer lead from this single operation contains about 11 oz., and similarly any lead to hand of this assay s added to the metal obtained by this operation. A second charge is next introduced into the pot in which the first operation was conducted and the separation effected, as before, into poorer ead and enriched bottoms, the former being transferred to the left hand and the latter to the next pot on the right. The poorer lead s similarly treated, and from it a further quantity of still poorer lead is produced, which s passed on to the next pot to the left and so on until the lead which reaches the market pot contains only 10 dwts. of silver per ton; the enriched lead meanwhile makes its way to the *rich pot,* but in the richer pots the separation s less complete than in the poorer ones, and the enrichment is not so rapid. In working the last pot, after two-thirds of the metal in the form of crystals have been transferred, the enriched bottoms, partly liquid and partly solid, are pressed with the back of the ladle. The fluid portion, richer in silver, runs through the holes in the ladle and is removed by an ordinary ladle. Working in this manner a market lead is obtained at one end of the range in which the silver is reduced to the amount already stated, and at the other end of the range is produced lead containing from 600 to 700 oz. of silver to the ton, beyond which it is not possible to push the concentration by this method.

In the above description it has been assumed that the method of thirds or the high system is employed. This is the method most usually adopted in practice, but for special purposes the low system or method of eighths is sometimes used, in which seven-eighths of the contents of the pots are transferred to the poorer pot. In some works the method of seven-eighths is used for 'riching up' rich leads to the refinery grade of about 600 oz. In the seven-eighths system the lead should treble itself in assay at each operation, but this is seldom the case. In the two-thirds system each operation is supposed to result in the doubling of the silver content of the lead, but in practice this only obtains with leads ranging downwards from about 50–60 oz. of silver per ton.

At each melting of the lead the metal is oxidised and a layer of dross formed on the surface. This is removed by skimming and the drosses collected for future reduction. With a 20-oz. lead, the amount of drosses formed is 25 p.c. of the weight of the metal. The continual drossing of the metal naturally effects a purification of the lead, as the dross produced consists not only of lead oxide, but also of the oxides of other easily oxidisable metals present. The value of the Pattinson process as a means not only of enriching the lead, but also of purifying it, is shown by the fact that lead to be used for white-lead making is frequently pattinsonised, although the amount of silver present may be very small. Further, copper and iron are both separated with the silver in this process when the amount of copper does not exceed 0·025 p.c.

The Rozan process or Pattinsonising by steam.—This process was introduced in the works of Luce and Rozan at Marseilles, and was first practised in England at Cookson's works on the Tyne. In this system steam under pressure is forced into molten lead, and by the continual agitation of the mass produced in this manner the production of crystals poor in silver is favoured, and the separation of an enriched fluid lead facilitated. Cookson was inclined to the opinion that the steam serves a second purpose, producing a chemical effect and aiding in the oxidation of the antimony, copper, iron, and arsenic, and other oxidisable metals present. This oxidation may be due to the air carried into the pot by the steam. In any case rich leads containing as much as from a ½ to ¾ p.c. of foreign metals may be treated by this system without having been previously softened. The following is the description of the plant and mode of working taken almost *verbatim* from Cookson (Trans. Newcastle Chem. Soc. 1878):—

The pot marked M (Fig. 19) is simply a melting-pot, and the lower pot C is the working, or, as it is commonly called, the crystallising pot. To illustrate the working, we will suppose the C pot contains 14 tons lead crystals from a previous operation, assaying, say, 80 oz. of silver per ton, and the M pot 7 tons original lead of similar silver content already melted; a moderate fire is set away in the firegrate of the C pot, and the contents of the M pot are skimmed; the hot lead from the pot M is then run on to the warm crystals in the C pot, and, with the assistance of the moderate fire already referred to, the whole contents of this pot (now 21 tons) are rapidly brought into a melted and working condition, when the charge is carefully skimmed; the M pot is at the same time charged with 7 tons of lead containing about 40 oz. silver per ton of lead, as this will be the assay of the crystals resulting from the operation shortly about to commence in the C pot. The fire under this pot is next drawn, and a small fire under each of the

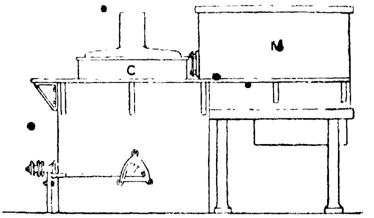

Fig. 19.

tapping spouts is set away, the object of this being to prevent the lead setting in them when tapping out the rich lead later on. Steam at 50–55 lbs. per square inch is next admitted through the valve v, and is distributed evenly through the pot by the baffle plate *b* (Fig. 20).

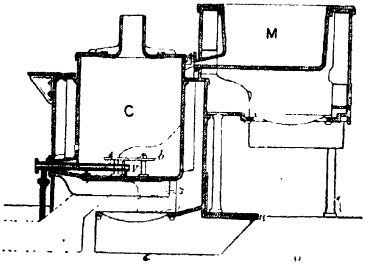

FIG. 20.

To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of the lead. This might be thought to cause the lead to set on the top, but the violent action of the steam entirely prevents this, and a more perfect crystallisation is effected than can be obtained in the old Pattinson process. When the workman sees that the charge is ready, *i.e.* when about two-thirds are in crystals and one-third liquid, he taps out through spouts at either side of the c pot the rich liquid lead, the poorer crystals being retained in the pot by perforated plates. This liquid lead is run into moulds containing 3½ tons each, and the blocks as they set are lifted out by cranes and arranged in a semicircle, where they await their turn to be again operated on. This process of crystallising, as in that of Pattinson, is repeated until the crystals are sufficiently poor in silver not to require further treatment, when, being fit for market lead, they are melted and run into pigs of the usual size, or into 3½-ton blocks, according to the purpose for which they are required; the rich lead is worked up until its silver contents are of the standard fit for the refinery. A large portion of the foreign metals contained in the original lead is skimmed off in the state of oxides; those from the richer charges are very dark in colour, some in fact almost black, owing to the impurities contained, while those from the poorer charges have the yellowish colour proper to the oxides of lead. Some, however, are carried off up the funnel above the c pot, with the escaping steam, and are deposited in the condensing chambers, of which there are several of large size. The dust contains 80–85 p.c. of lead oxide, a considerable amount of copper and antimony, and small quantities of arsenic, iron, and other metals.

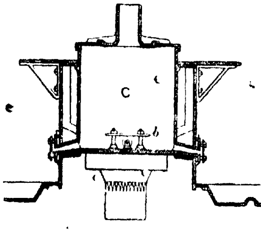

FIG. 21.

In the accompanying illustration of the plant used in the Rozan process, Fig. 22 is the plan of a battery, Fig. 19 is an elevation along the line S T, Fig. 20 a section along a line U V, and Fig. 21 a section along the line X Y.

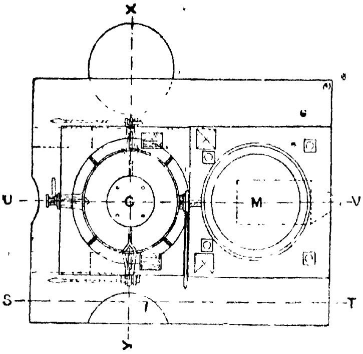

FIG. 22.

The following table gives the silver assays of twelve crystallisations taken from an average of 350 operations:—

Ounces per ton of lead

570-315-202-112 5-62-33 75-19 5-10-5-2 5-1·25-14 dwts

Cookson summarises the advantages of the Rozan system as follows:—

'1. The entire saving of the cost of calcining all ordinarily hard leads, and a very large saving in the case of especially hard leads.

'2. A cost for labour not exceeding one-fifth.

'3. A cost for fuel of about two-fifths.

'4. A saving of one-third in the oxides produced, which advantage any lead manufacturer will fully appreciate.

'Its defects are:

'1. A large capital outlay.

'2. A constant expense in repairs and renewals.'

At Omaha there is a modification of the Rozan process, introduced by Tredinnick. The pots, of which there are twelve, hold 50 tons, and each is supported by hydraulic rams, so that it can be raised and the lead or enriched alloy run into a neighbouring pot. There are two outlets to each pot, one fitted with a strainer for running off the alloy from the lead crystals, the other having a free run for pouring out the re-melted crystals. Heating is by gas, which is burnt in brick-lined jackets under the pots and the molten lead is stirred with steam, as in the Rozan process.

One advantage of this method is that the tapped lead does not require re-melting. Much time and labour are thus saved. The operation is done in about 40 minutes.

Newnam, in America, has recently adopted the Tredinniok method for the removal of bismuth from lead rich in that metal, and has been able to reduce the bismuth content of the lead to about 0·03 p.c.

The Parkes Process.—The method of desilverising lead by means of zinc is now very widely used. It has practically replaced all other methods, and is especially advantageous with leads rich in silver. Patents for this process were granted to Alexander Parkes, of Birmingham, in the years 1850, 1851, and 1852; and in 1859 the method was put in practice at Llanelly. It was subsequently tried at Tarnowitz, and, owing to the difficulties experienced in its working, finally abandoned at both places. The chief difficulties were (1) the removal of the zinc from the desilverised lead, which could not be performed sufficiently well to make the lead marketable; (2) the separation of the silver from the zinc alloy was attended by considerable loss; (3) the recovery of the zinc from the rich lead was somewhat difficult to accomplish. These difficulties have now been in great part overcome.

In brief outline, the process consists of the following operations: Zinc is dissolved in molten argentiferous lead. A light alloy, rich in zinc and containing most of the silver, rises to the surface, solidifies before the lead, and is removed as a solid crust. From this crust the zinc is recovered by distillation and the residual lead-silver alloy is cupelled. The desilverised lead contains a little zinc (about 0·6 p.c.) and is refined to produce market lead.

The relations to one another of the three metals concerned in the process merit further consideration. Silver mixes in all proportions with lead and zinc; lead and zinc, however, are only partly soluble in each other, the degree of solubility increasing with the temperature. Thus, if enough of each metal for mutual saturation be mixed (in the molten condition), separation into two layers takes place, the upper consisting of zinc saturated with lead, the lower, of lead saturated with zinc. For example, if 10 parts by weight of lead and 1 of zinc are mixed at a temperature of 350°, the distribution of the metals (p.c.) in the two layers is as follows:—

	Lead	Zinc
Upper layer . .	0·1	8·5
Lower layer . ..	90·9	0·5

Now, if silver be added to the molten lead and zinc, it is distributed between the two layers, dissolving preferentially in the zinc, so that the upper layer contains most of the silver. The following table (C. R. A Wright, Proc. Roy. Soc. 1892, 50, 390) shows the composition (p.c.) of the two layers in three experiments with the triple alloy:—

	Upper layer			Lower layer		
	Lead	Zinc	Silver	Lead	Zinc	Silver
1 . .	3·1	58·0	38·9	96·7	2·0	1·3
2 . .	3·4	51·6	45·0	96·4	1·9	1·7
3 . .	4·2	40·9	54·9	93·2	1·3	5·5

In example 1, the lead, zinc, and silver are mixed in the proportion by weight 5 : 3 : 2; a simple calculation from these data shows that the weights of the two layers are practically identical; now the ratio of silver in the upper and lower layers is 38·9 : 1·3, that is, 30 : 1; or, in other words, about 96 p.c. of the silver has passed into the layer rich in zinc. Similar relations hold in the other two examples and generally. The practical utilisation of this behaviour of the alloys in the desilverisation of lead is rendered possible by the solidification of the upper layer at a higher temperature than the lower one, so that the crusts, rich in silver, can be easily removed from the still molten, partly desilverised lead.

It will be evident that complete desilverisation of lead by this process is impossible; but if the extraction with zinc be repeated two or three times, the amount of silver remaining in the lead is commercially negligible, being of the order of ¼ oz. per ton.

Under similar conditions of treatment, gold behaves like silver, but is even more readily taken up by zinc, so that by using a small quantity of zinc in the first treatment the gold can be concentrated in the first crust and removed, leaving the bulk of the silver in the residual lead; *e.g.* 200–300 lbs. of zinc added to a 35-ton charge removed nearly 2 oz. of gold per ton of lead, along with the copper. The clean separation of the rich alloy from the lead is, of course, impossible in practice; much lead is carried mechanically with the crusts, even when these are squeezed in the Howard press. Poor crusts are often enriched by adding them to fresh baths of silver-bearing lead. The composition of a suitable crust for distillation is generally reckoned at 80 p.c. lead and 20 p.c. zinc and silver. An actual analysis of a crust may be quoted as typical:

Lead . . .	70·30 p.c.
Silver . . .	3·65 ,,
Zinc . . .	19·34 ,,
Zinc oxide . . .	2·05 ,,
Antimony . . .	1·11 ,,
Arsenic . . .	0·73 ,,
Copper . . .	2·25 ,,
	99·43 ,,

The relatively large amount of copper shown in this table is an indication of the ease with which that metal is extracted from lead by means of zinc. In this respect it stands on a level with the precious metals, and its presence is undesirable, as it increases the consumption of zinc. Arsenic and antimony have a similar effect, so that lead has to be thoroughly refined before treatment by Parkes' process.

The process is carried out in cast-iron pots or kettles, each separately fired, holding 25–60 tons of lead. Two of these, worked alternately, are used, and two smaller liquating or draining pots for the reception of crusts are generally arranged alongside of them. The diameter of a 30-ton pot is about 9 feet, and the depth is 3 feet 4 inches. When it is customary to syphon the molten lead, the depth of the pot is naturally limited by the height of the barometric column of lead.

The lead is usually run direct from the softening furnace and skimmed in the pot, though some desilverisers prefer to cast the softened lead into pigs and re-melt these in the zincage pots, since, thereby, better liquation and removal of copper is effected and zinc is economised.

The metal is heated somewhat higher than forming a receptacle for the molten metals. It has been proposed to mould these tests by presses worked by hydraulic power. The test before use is allowed to dry in the air for some time and then placed on an iron waggon and run into position under the furnace; it is then wedged tightly against an iron ring built in the masonry. The fire is next lighted, and the test slowly heated, so as thoroughly to anneal it. When perfectly dry, the temperature is raised to a dull redness and the test is filled with rich lead. The lead is first covered by a greyish dross, which, as the temperature rises, gradually gives place to litharge. The blast is now turned on and the oxidation of the lead takes place; the litharge produced is blown by the blast to the mouth of the refinery and flows over the gate into an iron pot, placed below. These iron pots are built on wheels, and when filled with litharge are removed; the cake of litharge is easily detached after cooling, and is subsequently reduced, as will be described later on. As the oxidation proceeds, fresh lead is added to the test, and if a large stock of rich leads have to be treated, then the refining is only conducted sufficiently far to produce an enriched alloy, in which the silver amounts to about 8 p.c. of the contents of the test. The concentrated argentiferous lead is tapped into an iron pot run on wheels, placed under the test bed, which is pierced by a drill. When the enriched lead has been run off, the hole is made up with a pellet of bone ash kept in its place by an iron plate, and another charge is introduced. By this removal of the enriched lead, distribution of silver through a large quantity of litharge is avoided. The rich lead is finally refined in another test. The end of the operation is indicated by the appearance of the surface, the brightening of the plate, as it is called; the blast is then turned off and the fire removed from the grate. The silver is usually tapped out into ingots direct, through a hole in the bottom of the test. In some cases the plate of silver is allowed to set, and when this has taken place the wedges are withdrawn and the test is lowered on to an iron waggon, by which it is removed and allowed to cool. The plate, when solid, is detached from the test, and brushed with an iron brush to remove litharge, slag, or material from the test.

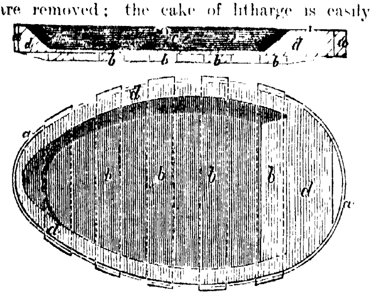

FIG. 25.

In an ordinary refinery 4–5 cwt. of lead can be worked off in an hour with a fuel consumption of 6–7 cwts. of coal per ton of lead oxidised. The plate of silver varies in weight from 10,000 to 20,000 oz., and is usually pure, containing about 99·7–99·8 p.c. of silver. The test bottoms are saturated with litharge and contain some silver; they are usually broken up and those portions free from lead picked out to be used over again, whilst the remainder is smelted in a blast furnace.

The German Method

In Germany the rich argentiferous lead is cupelled in a furnace known as the *Treibofen*, consisting of a reverberatory furnace with a circular hearth, and having a fireplace at one side. The bottom of this furnace is not movable, as in the English refinery, but composed of firebricks, on which lies a solid stratum of slag, and this again is covered by a coating of marl, well beaten down with iron rammers. The bottom is regularly hollowed out from the sides towards the middle, where a hollow is cut about an inch deep for the reception of the silver. The layer of marl is renewed for each operation. A dome of iron, plastered over with marl, covers the bed, and is moved as required by means of a crane. There are five openings into the side of the furnace, one serving to admit the flame from the fireplace, two smaller ones, near together, for the tuyeres by which the blast of air is forced on to the surface of the metal, and the litharge produced is blown towards a fourth opening, by which it escapes in a fused state. The tuyeres are usually provided with valves, 'butterflies,' which serve to diffuse the blast over the surface of the metal. The fifth opening into the furnace is provided for the introduction of the lead. In working with unsoftened lead the charge for one operation consists of about 5 tons of metal, some three-fourths of which is introduced into the furnace before lighting up, the remainder being added from time to time as the cupellation proceeds. Much larger charges are treated when softened lead is used. The mode of working is as follows: the charge of lead, in the form of pigs, is piled up in the middle of the hearth, and covered with wood, which is ignited by throwing on to it some burning charcoal. The iron dome is next let down and luted all round with clay. The blast is turned on and the fire in the grate made up. In the course of 3 or 4 hours the lead has melted down and the bath is covered by a layer of dross, which is dark in colour and consists of a mixture of the oxides of the metallic impurities contained in the lead, and is called the *abzug*; it is raked out at the opening for the removal of the litharge. After the removal of the *abzug* the surface of the metal becomes clearer, and in a short time acquires a peculiar circular movement; the dross now rising to the surface is purer and more fluid than the *abzug*. This second product forms what is known as the *abstrich*, and is an impure litharge, which, as it is produced, flows through channels cut in the breast of the furnace. The temperature is kept sufficiently high to maintain the *abstrich* in a state of fluidity. The formation of *abstrich* is succeeded by the production of pure litharge, which flows out of the furnace through the channels already mentioned. After the litharge-stage has commenced, the remainder of the metal to be cupelled is added in small portions at a time; the pigs of lead being so placed that the lead gradually melts and leaves behind the more refractory *abzug* unmixed with the metal. The full charge of metal having been added, the oxidation is continued and the temperature maintained sufficiently high to keep the silver in a molten state until the greater portion of the lead has been oxidised and the bright metallic surface of the molten silver is observed. The blast is then turned off and the fire is damped down; water is also thrown on to the metal to harden it, and the cake of *blicksilber* is withdrawn from the furnace and freed from marl, litharge, &c. The *blicksilber* contains from 90 to 95 p.c. of silver and is refined in a small reverberatory furnace, the bed of which is made of bone ash, or some material serving, like bone ash, for the absorption of litharge.

The cupellation of a charge of 10–15 tons of lead lasts from 70 to 80 hours, and the loss of metal amounts to 3–6 p.c.

Reduction of Litharge and Pot Dross.

The litharge produced in the cupellation of argentiferous lead, and the drosses formed in the Pattinson process, are reduced in this country in a reverberatory furnace, the sole of which slopes from the fire-bridge to a point near the flue, where an iron gutter, built in the furnace bed, serves to convey the molten lead to an iron receptacle outside the furnace. The reducing agent is coal. The sole of the furnace is prepared by covering it with small coal which is partially coked by the heat, and thus a porous covering is formed on the brickwork of the furnace bottom. On to this sole the litharge broken into lumps and mixed with coal is thrown. The fuel and the reducing gases in the furnace soon effect a reduction of the litharge, and the molten lead trickling through the porous mass gradually finds its way into the metal gutter, by which it is conveyed to the metal pot. The charge is turned over from time to time, and when the reduction is completed the residue, termed *cinders*, is raked out. The litharge cinders, together with other lead refuse, such as test bottoms, are smelted in a cupola, slag-hearth, or blast furnace.

The lead produced by reduction of litharge is softened and desilverised when necessary, and since the litharge produced towards the completion of the cupellation is richer in silver than that formed in the earlier stages, it is frequently reduced apart from the rest, and yields a lead containing from 70 to 100 ozs. of silver per ton. According to Kohlmeyer (Chem. Zeit 1912, 36, 1079), silver dissolves as oxide in litharge; the solubility is 3–6 p.c., and the melting-point of the litharge is reduced 45°.

Refining lead by electrolysis.—A process, due to Keith, for refining lead by electrolysis, was in use at New York for some years, but was, apparently, not a commercial success. The anodes were made of furnace lead, the cathodes of pure lead, and the electrolyte was a solution of lead sulphate in ammonium acetate. The bath was heated to 38°. The lead bullion contained 180 ozs. of silver per ton, the refined lead only 11 grains per ton.

Amongst other electrolytic methods of refining lead that devised by Betts is of special interest. The electrolyte is a solution of lead fluosilicate, a stable salt, easily made and very readily soluble in water. On electrolysing the solution of this salt, there is no formation of lead peroxide or other compounds which give rise to polarisation. The electrolyte is made by percolating broken quartz in a vat with 35 p.c. hydrofluoric acid. The resulting hydrofluosilicic acid is then allowed to act upon white lead; lead fluoride and lead sulphate settle out. The electrolyte is made to contain 5 p.c. of the lead fluosilicate and 10 p.c. of free hydrofluosilicic acid. It loses strength slowly and has to be made up weekly by the addition of fresh solution. Lead is deposited at the cathode in crystalline form, and as the crystals grow they are apt to cause short-circuiting; further, the mesh of crystals encloses electrolyte and thus renders the lead impure. This is obviated by the addition of a little gelatine to the bath; a compact deposit is then obtained of a high degree of purity.

At Trail, B.C., where the method is employed, there are 408 electrolytic cells made of cement and lined with asphalt, with a capacity of 100 tons of lead a day. The anode slabs are cast at the blast furnace; they weigh 320 lbs., and are reduced 80 p.c. in weight before melting again. The starting or cathode sheets are 39 by 27 inches and $\frac{1}{32}$ inch thick, and are made by pouring molten lead over an inclined steel plate. They are wrapped round copper bars connected to the negative leads, and are taken out and stripped twice during each run. The current density is 12 amperes per square foot, and the temperature is maintained at 30°–35° by cooling with water pipes.

The anode slimes contain 8000 ozs. of gold and silver per ton, and in addition copper, antimony, bismuth, arsenic, and lead (10 p.c.). They are washed, pressed, melted in a small reverberatory on a basic hearth, the slag removed, and the doré parted by sulphuric acid.

The only metals which pass into the electrolyte are zinc and iron, the latter to a limited extent. Bismuth remains with the anode mud. The refined lead is very pure, as testified by the following analysis: gold, 0·0027 oz.; silver, 0·6126 oz. per ton; copper, 0·0026 p.c.; iron, 0·0068 p.c.; antimony, 0·0075 p.c. The following table illustrates the gathering of the silver and the impurities in the anode slimes:—

	Lead (p.c.)	Copper (p.c.)	Bismuth (p.c.)	Antimony (p.c.)	Arsenic (p.c.)	Silver (p.c.)
Lead bullion	87·14	1·40	4·14	4·0	7·4	0·64
Refined lead		0·001	0·0022	0·0017	tr.	—
Anode slimes	10·13	9·3	0·52	25·32	44·58	4·7

Viewed as a desilverising process, the electrolytic method is probably superior to any of the others; it has the advantage, too, of eliminating bismuth from the lead. (For further details, *see* A. G. Betts, Lead Refining by Electrolysis, J. Willy & Sons, 1908; T. A. Rickard, Min. and Scient. Press., Dec. 23, 30, 1916.)

Condensation of Lead Dust and Fume.

In consequence of the volatility of lead at high temperatures a certain proportion of the metal and some of its compounds are carried away by the heated gases in the operations of smelting, refining, &c. Most lead ores contain zinc and arsenic, both easily volatile, and readily oxidised metals; these, therefore, bulk largely in the fumes from lead works. Solid material from the ores and fluxes is carried over mechanically in the form of a fine powder. This constitutes the 'dust'; it settles out more easily than the fume. Naturally, there is no hard and fast distinction between dust and fume, but the latter may be taken, in a general way, to consist of the compounds (oxides, sulphides, and sulphates) produced from the volatilised metals from the furnace charges. A certain proportion of silver is always found in fume lead, the amount being considerably less than in the ores from which it is derived. To prevent the loss and minimise the nuisance which would arise from allowing the gases produced in these various operations to pass direct into the chimney, the furnaces are connected with a series of flues or condensing chambers in which the gases are cooled and so deposit some of the solid matter held in suspension, before they issue from the chimney. These flues are cleaned out at intervals, and the 'fume' collected

The method of fume condensation usually relied on is simply to connect up the smelting and other furnaces with long flues of large transverse area. In some establishments they have an aggregate length varying from 3 to 5 miles, and a cross section of from 6 feet by 7 feet to 8 feet by 9 feet Sometimes they are spiral or zig-zag to economise space, and baffle walls are interposed to lengthen the path of the gases and expose a large surface for precipitation of the fume. Sheet iron plates, hung longitudinally, and parallel rows of iron wires in vast numbers are among the methods which have been tried, though with limited success, to effect precipitation of the solid particles

The following are analyses taken from Percy's Metallurgy of Lead (p. 451) of dust and fume from the flues of the reverberatory furnaces and slag hearths at Bagillt:

Lead oxide . .	46·51	62·26	46·88
Lead sulphide .	4·87	1·05	-
Ferric oxide and alumina	4·16	3·00	10·00
Zinc oxide	1·60	1·60	4·14
Lime	6·07	3·77	6·73
Sulphuric anhydride .	26·51	25·78	14·15
Insoluble residue . .	10·12	1·97	14·40
Carbonaceous matter .	—	—	3·37
	99·87	99·43	99·67

The amount of flue-dust recovered is 4 p.c. of the ore at Pertugola, 4·7 p.c. at Tarnowitz, and 4·8 p.c at Freiberg. It is usually briquetted with lime and clay and added to blast-furnace charges. At Freiberg, the average composition is: lead, 35·4; arsenic, 14·1; silver, 0·0276 p.c. Lead averages 40 p.c. in the flues near the furnaces; it decreases to 30 p.c. and then rises to 36 p.c. beyond the point where lead oxide is condensed; arsenic increases regularly, with the distance, from 7 to 25 p.c. The treatment at Freiberg depends on the arsenic-content. When this is below 7 p.c. the dust is briquetted and smelted with ore; when between 7 and 15 p.c. it is roasted before briquetting, and when over 15 p.c. it is roasted to recover arsenic and the residue smelted.

Jets of steam and water have in some cases been introduced at different points in the flues with the object of facilitating the fume deposition; but lead smelters differ in opinion as to the advantages gained by the use of either steam or water. Various devices have been proposed to effect a condensation of lead fume without the necessity of constructing long flues or large condensing chambers.

Stagg's condenser consists of a large rectangular chamber divided by partitions springing alternately from the top and bottom of this chamber, leaving free spaces above and below; the lower part of the chamber is filled with water, so that the gases pass first down one side of a partition through the water, and rising in the next compartment pass over the next partition and down again through the water. The gases are drawn through the chamber by means of air-pumps attached to the exit flue. The fume in its passage through the condenser is thus drawn through water and robbed of part of the suspended solids.

Stokoe's condenser consists of two chambers divided into several compartments by partitions which alternately reach the top and dip below the surface of water at the bottom of the chamber. The chamber is divided horizontally by two floors made of open joists upon which faggots are laid, thus forming filtering beds, which are washed by water in the form of fine spray. The gases are forced through the compartment of the condenser, meet the fine spray of water, and pass through the filtering beds, where the fume as it collects is washed away. When the water has reached a certain height it is drawn off into tanks, where the solid matter gradually separates.

In 1878 Messrs. Wilson and French patented a condenser, which was adopted at the Sheffield Smelting Company's works, and by Messrs. Bewick and Partners, Limited, of Hebburn-on-Tyne. The condenser consists of a wooden box *aa*, Fig 26, having a shelving bottom where the solid matter collects, and at the lowest point a tap, *b*, by which the contents of the condenser are run off from time to time. The box is filled with water to the level of *c*. The gases are forced into the box by a fan, along the pipe *h*, which opens into a chamber *g*, formed by a partition running parallel with the side of the box. Below, this chamber opens into a series of triangular tubes *i*, running across the box; these tubes are perforated above, and through

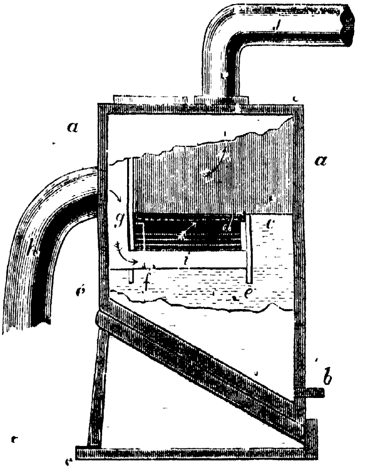

FIG. 26

the fine openings the gases are forced into the water. Near the surface of the water at *d* are fixed three or four screens made of wickerwork or copper wire, held in position by the supports *e* and *f*. The gases pass out finally by the pipe *j* in the top of the box, and are conducted by flues to the chimney. By this arrangement intimate contact between the water and the particles of the fume is insured. The fume collects in the lower part of the box, is drawn off into settling tanks, and after removing the greater portion of the water, is dried and smelted. With three wire-gauze screens and a depth of 8½ inches of water, Mr. French states that at the Sheffield Smelting Company's works, the quantity of lead and silver arrested amounts to from 95 to 98 p.c. of that contained in the smoke as it leaves the furnace.

Wet methods of fume-condensation have proved unsatisfactory. Recent progress in this field has been along two lines, viz. · filtration and electrical precipitation, the fume in each case being operated on in the dry condition.

The suggestion of Percy, in 1870, to filter the fume through cloth was worked out on a practical scale by Lewis and Bartlett, and has been extensively developed. The filters are in the form of bags, 30 feet long and 16 inches wide, made with one lateral seam. The material is either cotton or wool, the latter being found more serviceable, especially when the natural oil and sweat have not been removed by washing. Hundreds or thousands of these bags are hung in a brick chamber or bag house; the tops are tied tight, the bottoms fit round holes in the floor of the house. Under the floor is a smaller chamber into which the furnace gases are forced by fans. The gases escape upwards, are filtered through the bags and pass into the open air through ventilators in the roof of the bag-house. The fume is detached from the fabric periodically either by shaking the bags or by causing them to collapse by suction. It falls to the lower chamber and when a layer 2 feet thick has collected the furnace gases are diverted and the powder is ignited by a small fire. The fume, containing much oxidisable matter, burns easily and yields a grey cinder suitable for smelting in the blast furnace.

At the Murray Plant, Utah, the bag houses are 216 by 90 feet and 90 feet high. There are 4000 bags with a surface area of 570,000 square feet, which cope with 165,000 cubic feet of gas per minute, *i.e.* 1 cubic foot of gas passes through 3·5 square feet of filter per minute. Fig. 27 is a diagram of a bag-house at the Globe Smelting Works, Utah. It is stated that 1000 square feet of filtering surface are necessary, in general, for one ton of ore, and the best temperature for filtration is variously given as 80°–120°C. Gases from roasters are not suitable for bag-house treatment, as the oxides of sulphur rot the fabric. The life of cotton bags at Utah is 17 months and of woollen bags 4 years. At these works, 1·27 p.c. of the lead and 0·063 p.c. of the silver in the charge are recovered from the bag-house, and the fume contains: lead, 52·5; arsenic, 14·2; sulphur, 5·4; zinc, 3·0; antimony, 1·6 p.c.

At St. Louis, hearth-smelting yields twice as much bag-house fume as flue-dust. The burnt fume contains 76 p.c. lead and 5·9 p.c. of sulphur; the dust, 62 p.c. lead and 11·1 p.c. of sulphur. The lead in these products is combined as follows (Newnham, *loc. cit.*):

	Flue dust (p.c.)	Burnt fume (p.c.)
Lead sulphate . .	18·9	53·6
Lead sulphide . .	55·4	1·2
Lead oxide . .	2·0	41·5

The application of electricity to fume condensation was suggested by Sir O. Lodge, and its use patented by Walker. Experiments made in 1885 by Hutchings, using a power-driven Wimshurst machine and a system of metallic points, at the Bagillt works of Messrs Walker, Parker & Co., Limited, yielded satisfactory results when working on a small scale, but did not prove successful when applied to the flues of the works.

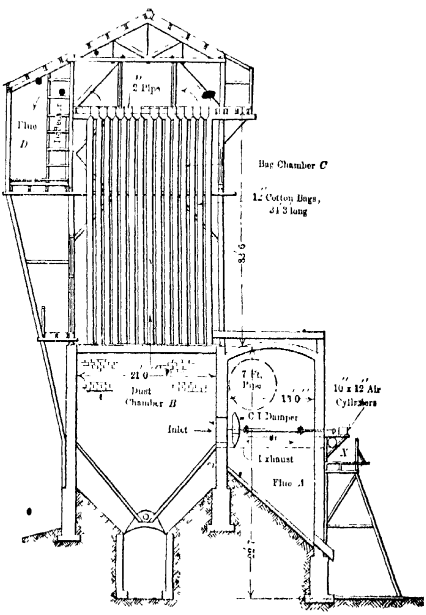

FIG. 27.

(*From* Hofman's 'Metallurgy of Lead.')

The development of these early ideas and methods has been due, in great measure, to the labours of F. G. Cottrell (*see* Smithsonian Report, 1913, pp. 653–685). In the glow discharge of electricity from points at high potential, particles in the neighbourhood of the points receive an electrical charge and are repelled. If an earthed plate, or one of opposite polarity, be brought near, the particles are attracted, precipitated on the plate, and lose their charges. It has been found by experience that a high, direct-current voltage is preferable to an alternating one for the precipitation of dust and fume. The ordinary low-voltage alternating current generally available is thus transformed, for this purpose, into high-voltage alternating and then into intermittent high-voltage direct current. Some of Lodge's recent patents are concerned with the rectification of alternating currents by means of vacuum tubes, which allow the current to pass only in one direction.

In the process, as carried out at present, the discharging electrodes, negatively charged by preference, have a voltage of 75,000 to 100,000. They consist of iron chains carefully insulated, which are hung in the middle of steel pipes 15–20 feet long and 10–18 inches in diameter, through which the gases are drawn. The 'collecting' electrodes, the pipes, are earthed and the precipitated fume is shaken down at intervals by striking them with a hammer.

A Cottrell plant at Trail for the treatment of 100,000 cubic feet of gas per minute consists of 384 pipes. The velocity of the gases for pipes of 12-inch diameter should not exceed 3·5 feet per second.

Fractional precipitation of fume, consisting of materials differing in volatility, is possible by the Cottrell process when operations are carried out at different temperatures. Thus, high grade white arsenic can be separated from lead fume by electrical precipitation of lead and zinc compounds at a temperature at which white arsenic is gaseous; on cooling the escaping gases, the oxide of arsenic becomes solid and can be recovered by repeating the electrical treatment.

Gases from reverberatory and blast-roasting plant which are unsuitable for bag-filtration, owing to the injurious effect of the gases on the cloth, can be treated without difficulty by the Cottrell method, and it would appear that this method had a great future in store, not only for the treatment of lead fume, but also of many kinds of dust, mist, and smoke, which are produced in numerous large-scale operations.

PROPERTIES AND USES OF METALLIC LEAD.

Owing to the demand for soft lead in many industries, and the hardening effect of minute quantities of foreign metals on lead; owing, also, to the need of purifying the metal before desilverising and to the refining action of the desilverisation-process itself, commercial leads are usually of a high degree of purity. The following table of analyses of some commercial leads shows the nature of the chief impurities and the extent to which they are present:

——	Best English lead	Good chemical lead	Ordinary English lead	B H P Australia special market lead	B.H P Australia ordinary market lead	Electrolytic lead, Trail, B C.
Lead	99·9919	99·985	99·9655	99·9977	99·9917	99·9861
Copper	0·0003	0·022	0·0019	0·0003	0·0001	0·0027
Antimony	0·004	0·033	0·0132	0·0005	0·006	Nil
Arsenic	Nil	trace	Nil	—	—	0·0025
Bismuth	0·0005	0·001	0·0124	0·0006	—	0·0037
Silver	0·0003	0·002	0·0007	0·0002	0·0012	0·001
Iron	0·0015	0·003	0·0031	—	—	0·0022
Manganese	Nil	—	Nil	—	—	—
Nickel	Nil	trace	trace	—	—	—
Cobalt	Nil	—	Nil	—	—	—
Zinc	0·0015	0·001	0·0026	0·0007	0·001	0·0018
Cadmium	Nil	—	0·0006	—	—	—
Tin	Nil	—	Nil	—	—	—
	100	100	100	100	100	100

Lead is a bluish-grey metal, the freshly cut surfaces exhibiting a distinct metallic lustre, which soon disappears owing to superficial oxidation. Its crystalline character is well shown by the beautiful fern-like crystalline growths which are seen on the pigs of best market lead, or as they form on the surface of a casting during the cooling of the molten metal. It can easily be obtained in the form of regular octahedrons by melting lead, allowing the molten metal to solidify partially, and pouring off the portion still remaining liquid. It is deposited in arborescent forms, known as the lead tree, by the decomposition of a solution of lead acetate either by zinc or by electricity. Lead is a very soft metal, easily cut by a knife or scratched by the nail; it readily receives impressions and leaves a streak on white paper. Its hardness is 1·5 on Moh's scale. It is very malleable and is ductile. Rolled lead is more ductile than cast lead; both its malleability and ductility are injuriously affected by the presence of impurities. Lead is a metal of feeble tenacity, a wire $\frac{1}{12}$th of an inch will not support a weight of 20 lbs. When struck with a hammer pure lead emits a dull sound; the presence of antimony, however, makes it sonorous, hard lead being easily distinguished from soft lead by this property. The presence of antimony, zinc, arsenic, or silver increases the hardness and brittleness of the metal. Antimony makes the metal hard if present in amount over 0·005 p.c.; small quantities of bismuth are not injurious in this respect.

According to Schweitzer the sp.gr. of lead (Amer. Chem. J. 7, 174) varies between 11·344 and 11·377 at 4°. St. Claire Deville (Phil. Mag. [iv.] 11, 144) gives the following as the results of his observations on lead prepared in different ways:—(1) cooled slowly from fusion 11·254; (2) cooled quickly from fusion 11·363; (3) electrolytic lead, 11·542; (4) lead obtained by electrolysis, then fused and cooled quickly, 11·225. The mean may be taken as 11·35 at 20°C. The influence of pressure on the sp.gr. of lead is shown in the following results obtained by Spring (Ber. 16, 2724). (1) Not pressed, 11·350 at 14°; (2) once pressed, 11·501 at 14°; (3) twice pressed, 11·492 at 16°. The sp.gr. of molten lead is given as 10·37 and 10·65 by Roberts-Austen and Wrightson (Ann. Chim. Phys. [v.] 30, 181), and 10·952 by Quincke (Pogg. Ann.

135, 642). The increase in volume on melting is 3·5 p.c.; 1 cubic foot of solid lead weighs 710 lbs. and one of molten lead, 664 lbs. The melting-point is 327·4°; the boiling-point, that is the temperature of visible ebullition, is stated to be 1525°. The metal is only slightly volatile in the absence of air, but is carried over in considerable quantity by the vapour of zinc.

The specific heat of lead according to Regnault is 0·0314 at temperatures between 10° and 100° (other observers give 0·02925), and for molten lead according to Person it is 0·0402 between 380°-450°. The latent heat of fusion is 5·369 calories; the coefficient of linear expansion between 0° and 100°, 0·0000295; the conductivity for heat, 7·9, and for electricity, 7·8, compared to silver, 100.

Lead is tasteless; it is said to emit a characteristic odour when rubbed between the fingers. It can be welded in the cold by pressing the clean surfaces together.

An allotropic form of lead (or possibly more than one) was prepared by Cohen and Helderman (Zeitsch. phys. Chem. 1915, 89, 733) by suspending lead in 40 p.c. solution of lead acetate containing 10 p.c. nitric acid (D. 1·16). In these conditions the lead becomes wrinkled and denser. Three specimens of density, 11·3415, 11·3129, and 11·3283, were produced in this way from metal of density 11·3299. According to H. Heller (*ibid.* 761) this 'grey' lead is rapidly formed in solution of its acetate if only a little nitric acid be present. H. J. M. Creighton observed the formation of the same allotrope during the electrolysis of nitric acid (D 1·42) when lead formed the cathode (J. Amer. Chem. Soc. 1915, 37, 2034).

When lead is freshly distilled in silica vessels, it is rapidly attacked by water and oxygen, acting together. If, however, the distilled lead be kept some time *in vacuô*, it is much less easily corroded when brought in contact with water and oxygen. This curious behaviour has been accounted for by assuming that freshly distilled lead is not physically homogeneous, the varieties (allotropes) differing in their solution-pressures (B. Lambert and H. E. Cullis, Journ. Chem Soc. 1915, 107, 210). There are no observations as yet which correlate these allotropes with Heller's grey lead; indeed, the very existence of allotropes has been denied by some authors (A. Thiel, Ber. 1920, 53, 1052, 1066).

Speculations concerning the relationship of lead to the products of the radio-active changes of uranium and thorium have stimulated a great deal of interest in the question of the atomic weight of lead. Soddy has pointed out that the older determinations vary considerably. Thus, of 24 values given in Abegg's Handbuch, 19 range almost over a unit, viz.: from 206·8 to 207·6. Recent determinations give fairly consistent results for ordinary lead, but the values for lead derived from radio-active minerals vary considerably. A number of these results are given in the following table:—

	Source of lead	Atomic weight	Observer
1	Radio-active minerals, Colorado	207·00	Richards and Wadsworth
2.	,, ,, Australia	206·34	
3.	Bröggerite	206·12	
4.	Cleveite, Langesund	206·08	
5	Uraninite, N. Carolina	206·46	Richards and Lambert
6.	Pitchblende, Joachimsthal	206·57	
7.	Carnotite, Colorado	206·59	
8.	Thorianite, Ceylon	206·82	
9.	Pitchblende, England	206·86	
10.	Ordinary lead (control)	207·15	
11.	Uranium mineral	206·98	de Coninck and Gerard
12.	Ordinary lead (control)	206·71	
13.	Uranium mineral	206·36 to 206·64	Maurice Curie
14.	Monazite	207·08	
15.	Ordinary lead (control)	207·01	
16.	Thorium mineral ThO_2 62 p.c. U_3O_8 1·9 ,, PbO 0·39 ,,	208·4	Soddy
17.	Pitchblende	206·736	Hönigschmid and St. Horovitz
18.	Pitchblende, Joachimsthal	206·405	
19.	Uranium mineral, East African (formerly German)	206·046	
20.	Bröggerite U_3O_8 79 p.c. ThO_2 4·5 ,, PbO 9·5 ,, Norway	206·063	
21.	Ordinary lead (control)	207·180	
22.	Samarskite	206·30	Davis
23.	Thorianite, Ceylon	206·88–207·24	Hönigschmid
24.	Thorite, Norway	207·88–207·92	
25.	Spring water, Japan	207·13	Richards and Sameshima

The lowest value, 206·046 (No. 19) and the highest, 207·92 (No. 24) agree very closely with those calculated from the disintegration-theory for uranium-lead and thorium-lead, viz.: 206 and 208 respectively. Opinions differ as to the cause of the variable atomic weights, between these extremes, of the lead derived from radio-active sources. Such leads may be mixtures of ordinary lead and lead isotopes, or ordinary lea may be a distinct variety or a balanced mixtu of the isotopes derived from uranium an thorium, or finally it may be an evolutiona product from lighter materials (*see* F. W. Clark Proc. Nat. Acad Sci. 1918, 4, 181). Attemp *by Joly and Poole (Phil. Mag. 1920, vi. 39, 372) to separate ordinary lead into isotopes by centrifugalising the molten metal did not meet with success.*

The melting points of two varieties of lead, differing by 0·8 in atomic weight, were found by Richards and Hall to agree within 0·05°. The index of refraction and the solubility of the nitrates derived from test lead and lead of atomic weight 206·42 were found to be practically identical by *Richards and Schumb* (J. Amer. Chem. Soc. 1908, 40, 1403). Richards and Wadsworth, *however, found the density of* ordinary lead at 20° to be considerably higher (11·377) than that of lead extracted from Australian radio-active minerals (11·288); as the atomic weights vary proportionately to the densities, the atomic volumes are identical, viz.: 18·277 and 18·276. It is evident that the isotopes only differ from one another in respect to mass.

Lead is easily oxidised by exposure to the air, and in the finely divided state, as obtained by the decomposition of the tartrate by heat, is pyrophoric. It is not attacked by air-freed water, nor by dry air free from carbon dioxide, but easily suffers corrosion under the combined influence of air and moisture, or of water and air, lead hydroxide being produced. This dissolves in the water and is converted into a basic carbonate by the carbonic acid present. The action of water on lead is materially influenced by the presence of small amounts of salts: nitrates are supposed to further the action—this is especially true of ammonium nitrate—whereas chlorides, sulphates, carbonates, and phosphates retard the action. Chlorides, sulphates, and carbonates, especially the last, diminish the solvent action of nitrates and in some cases destroy it altogether. Water saturated with carbon dioxide under ordinary pressure has but little solvent action on lead, but under a pressure of six atmospheres, the solvent action is considerably increased. In this case also the presence of ammonium nitrate and of potassium carbonate tends to retard the action. These conclusions are drawn from the observations of Muir (Chem. News, 33, 102, 125, 145; 34, 223, 324), who has also studied the influence of salts on the solubility of the basic carbonate

$$(PbCO_3)_2,Pb(OH)_2.$$

The order of solubility of this compound agrees very nearly with that of metallic lead in solutions of the same salts (Muir, Chem. Soc. Trans 31, 660). The influence of small quantities of free sulphuric acid on the corrosion of lead by saline solutions has been studied by W. Carleton Williams (J. Soc. Chem. Ind. 6, 111). The presence of 1 grain per gallon of free acid notably increases the action. Allen (Chem. News, 46, 145) found that water taken direct from the main in one town in Yorkshire, and having an acid reaction, when left in contact with lead, dissolved an amount of lead equivalent to 0·42 to 0·56 grain per gallon, but after the water had been made slightly alkaline the amount of lead dissolved was equivalent to 0·14 grain per gallon only. Crookes, Odling, and Tidy ascribe the activity of water towards lead to deficiency of silica, and are of the opinion that from 0·5 to 0·7 part of silica per 100,000 is sufficient to prevent the action. In many cases *the corrosion of the lead pipes would appear to be due to the presence of a free acid in the water supply, as is apparently the case with one of the* water supplies of Sheffield, and also the water supply at Huddersfield (Allen, *l.c.*, also Chem. News, 46, 88). The waters most liable to act upon lead are those obtained from upland gathering grounds, waters which are soft and usually of remarkable purity. The presence of *peat in water increases its action on lead, except* when the water is permanently hard (H. Heap, J. Soc. Chem. Ind. 1913, 32, 847). The activity of such waters is by many attributed to the presence of free acid (*cf.* P. F. Frankland, J. Soc. Chem. Ind. 8, 241) (*v.* WATER).

Since air facilitates the solvent action of water, an intermittent water supply is favourable to the contamination of the water, and as lengthened contact with lead in the case of an active water will naturally result in a considerable proportion of the metal being dissolved, it is advisable to run off the water that has been standing over night in the pipes, as such water may be unfitted for drinking purposes.

Lead is dissolved easily by dilute nitric acid; the action of concentrated acid is soon arrested by the formation of a protective layer of lead nitrate on the surface of the metal. Dilute hydrochloric and dilute sulphuric acids do not attack lead, but it is dissolved by boiling concentrated hydrochloric and sulphuric acids, lead chloride and lead sulphate being formed.

Lead is largely used in building construction in the form of sheets, gutters, spouts, &c., also for the manufacture of pipes for gas and water, and of cables, accumulators, and rifle bullets. Its power of resisting the action of acids, &c., renders it of great service in the construction of chemical plant, *e.g.*, sulphuric acid chambers. The lead preferred for this purpose is obtained by remelting old lead, and is hardened by a small amount of antimony. Experiments of Johnson and Calvert (Compt. rend. 56, 401), of Hasenclever (Wag. J. 1872, 239), and of Bauer (*ibid.* 1875, 364) have shown that ordinary leads resist the action of sulphuric acid more effectively than pure lead. Lead is also an important constituent of many alloys, *e.g.* solder, type-metal, bearing-metal, fusible alloys, and pewter. Bullets for smooth-bore small arms are hardened with antimony to give them greater penetrating power.

Sheet lead.—For the manufacture of sheet lead, market lead is cast in a plate several inches in thickness. When the plate is somewhat cooled it is transferred to the rolling mill, which consists of a pair of massive iron rollers, about 18 inches diameter and 8 feet wide, which are worked by engines with reversing gear. The rolls are placed in the middle of a long bench, a little wider than the rollers, and about 3 feet high; at intervals of a foot along the bench are placed wooden rolls on the same level as the rollers, which serve to facilitate the movement of the sheet to and fro. By passing and repassing the plate between the rollers it is gradually extended into a sheet, which, when too long for manipulation in the ordinary way, is cut into smaller sheets which are rolled separately. Or the sheet may be doubled over, the surface being previously chalked to prevent the adhering of the two sheets, and the doubled sheet rolled out to the required thickness. The lead having been rolled out, the edges and ends of the sheets are cut straight and the sheet wound on to a cylinder at the end of the bench.

Lead pipes are usually made in machines worked by hydraulic pressure. Over the piston of the press is a reservoir which contains the metal, and which may be heated by an annular fireplace. The reservoir is filled with molten lead by a spout through an aperture in the top; when filled the spout is withdrawn and the aperture closed tightly by an iron plug, kept in position by an iron key. The size of the pipe is regulated by a steel die of the diameter of the outside of the pipe fitted at the top, the internal diameter of the pipe being determined by a mandril which passes directly through the centre and is moved upwards by the rising piston, the semi-molten metal being at the same time forced through the die. As the pipe passes out at the top it is coiled on to a drum. The pipes used for gas-services are sometimes made of metal to which either tin and antimony have been added directly, or these metals may be supplied by the addition of a harder lead containing them.

Lead shot is made by alloying the metal with arsenic (0·3–0·8 p.c.), which is added either in the form of white arsenic or arsenical dross from the improving furnace. The addition of arsenic serves to impart a greater fluidity to the metal and increases the tendency of the metal to assume a spherical form in passing through the air. With too little arsenic, the drops are pear-shaped; with too much, the shape is double convex. The molten metal is made to run through cullenders, and to fall a considerable height into water-butts. A small amount of sodium sulphide (about 0·025 p.c.) is added to the water to prevent oxidation of the lead. The height required for the fall is either secured by means of a shot tower, or by a deep well, the shaft of an old coal pit being in some cases adapted for this purpose. The size of the shot is determined by the size of the holes in the cullender, by the height from which the lead falls, and by the temperature and consequent fluidity of the molten metal.

The shot, taken from the vessel in which it has solidified, is sorted by sieving into different sizes, and the imperfect ones separated by causing the shot to roll down an inclined polished metal surface, or a wooden table sloping at 15°. The perfect shot acquire the highest velocity and shoot well over the edge of the table into a bin; the imperfect fall short of this and are gathered apart. The shot is finally polished by shaking with a little graphite in a cask revolving on a horizontal axis.

Lead Compounds used in the Arts.

Lead oxide, lead monoxide, or *plumbic oxide* PbO. The varieties of this compound are *massicot* and *litharge*, the former name referring, strictly, to the unfused, the latter to the fused, compound. The tendency, at the present time, is to use the term 'litharge' for all varieties of lead monoxide. The compound is obtained when molten lead is heated at a moderate temperature in a reverberatory furnace, the molten lead being constantly stirred. It is formed in the first stage of the manufacture of red lead. After grinding, levigation, and drying, it is obtained as a brownish-yellow powder, usually containing some metallic lead, lead peroxide, and grit. It is generally known, commercially, as ground litharge or massicot.

Litharge is produced when the oxidation of lead takes place at a temperature sufficiently high to melt the oxide formed, as in the cupellation process. When manufactured for sale, the purest lead is submitted to cupellation; if the lead used is not quite pure, then the portions of litharge first formed and that produced towards the end of the operation are rejected. The litharge as it forms is collected in large iron pots fitted on wheels, in which it is allowed to cool slowly. When the pots are emptied, the litharge 'falls,' the central portions which have cooled more slowly being somewhat lighter in colour and possessing a scaly crystalline structure. The more friable portion is broken up and passed through a circular temse or screen, and sold as *flake litharge*. That portion of the litharge which does not fall, but remains in hard coherent masses is ground between horizontal stones in a stream of water, run into settling tanks and dried at a low temperature in a reverberatory furnace. This is known as *levigated litharge*.

A mechanical furnace for making litharge was patented by Noad in 1895 and was modified and improved later by Barton and others. It consists essentially of an iron pan, fitted with a cover and stirring paddles and connected with fume-condensing chambers by an upright shaft. Molten lead is fed in through a side pipe during the operation. Lead is heated in the pan to a temperature of 600°C., stirred and splashed by the paddles and treated with a blast of steam and air, which enters through a pipe in the cover. The fume of finely divided lead and lead oxide, mixed with the gases, escapes through the uptake and passes to the condensing chambers. The litharge-dust collected in these is sometimes levigated to reduce the amount of blue lead in it, sometimes calcined at a high temperature and then sifted. Attempts have been made, by heating the uptake from the pan, to oxidise the blue lead in the effluent fume so thoroughly that subsequent treatment is not required.

The litharge obtained by this method is canary-yellow in colour and very fine in grain. It may contain as little as 0·05 p.c. insoluble in acetic acid and 0·005 p.c. insoluble in nitric acid, and is thus practically free from grit, metallic lead and lead peroxide. It is especially valuable for proofing fabrics and for conversion into pigments.

The colour of lead oxide varies from lemon-yellow to reddish-yellow, and on heating or exposure to light it becomes brownish-red. The yellow variety is also turned red by mechanical compression. The solubility of the red form is 0·029, that of the lemon-yellow 0·047 gm. mols. in normal caustic soda at 20° (Glasstone, Jour. Chem. Soc. 1921, 120, 1689). The sp.gr. of different varieties of lead oxide are given by Geuther (Ann. Chim. Phys. 19, [ii.] 60–61) as follows: yellow cryst. 9·29 at 15°; red cryst. 9·126 at 15°; red cryst. 9·125 at 14°; red powder, 9·09 at 15°; and red, very pure, 8·74 at 14°. The melting-point is variously given as 776, 879, 888, and 906°C Litharge is reduced by carbon monoxide at 100° and by hydrogen at 310°. It absorbs oxygen when molten and gives it up again on slow cooling, falling into powder the while. When fused with sulphur, iron, zinc, copper, antimony, and several other elements, it oxidises them and the oxides dissolve in the molten litharge, provided this is present in sufficient amount: Thus 1 part each of ferric oxide, zinc oxide, antimony oxide and tin oxide require 10, 8, 5, 12 parts, respectively, of lead oxide for complete solution and fusion. These properties of litharge are utilised in assaying silver ores and refining silver.

Litharge is used in the manufacture of flint glass; as a glaze for earthenware; for the preparation of lead acetate, lead nitrate, lead chromate, lead plaster, for drying oils, for proofing fabrics, and in the manufacture of rubber and electrical accumulators.

The occurrence of native litharge in Kurdistan has been described by Alex. Scott (Min. Mag. 1914, 17, 143). The mineral is red, with a yellowish-brown streak, and partly crystalline. The sp gr. is 8·61 and analysis shows it to contain PbO, 97·17; CuO, 2·61; Sb_2O_3, 0·30 p.c. E. S. Larsen (Amer. Min. 1917, 2, 18) also records the natural occurrence of crystalline litharge from Austria and California. The mineral is yellow and the constituent crystals are orthorhombic, biaxial, and optically positive. This is surmounted by a reddish fringe of tetragonal, uniaxial crystals, optically negative, which are regarded as native massicot.

Red Lead, Minium, or *Plumbic Tetroxide* Pb_3O_4. The manufacture of red lead is effected in two stages, the first being the conversion of the lead into massicot or the 'drossing' of the lead, and the second the conversion of the monoxide into red lead of the required shade. These operations are usually conducted in two different furnaces. The drossing oven, is a low-arched furnace with a bed of firebrick laid on a bed-plate of cast iron having raised borders on each side and at the back. The bed of the furnace is made to slope slightly towards a median line, and also from back to front. On either side of the furnace bed is a low wall, the spaces between which and the wall of the furnace form the two fireplaces. In front are three openings closed by hinged doors of cast iron; the two side ones communicate with the fireplaces, whilst the central one, which is larger than the other two, serves for the introduction and the working of the charge, and for the escape of the products of combustion, which pass into a hood of brickwork in front of the furnace, this hood forming the base of the short vertical chimney attached to each furnace. In front of the working door is hung a chain with a hook at the end; this serves as a fulcrum for the rabble used in working the charge. Below the working door a space is formed by two vertical plates of cast iron on brick walls, resting on a slab of stone or plate of iron on the floor, and supported by the iron plate which forms the lower part of the front of the furnace. This space in front serves to collect any of the oxidised product which may fall in transferring it to the waggons. The length of the furnace is about 11 feet, and the width between the bridges is about 8 feet 4 inches. The 'colour oven' is in most essentials similar to the 'drossing oven'; the bottom is flat and the slope from back to front not so great as in the latter Coal is used as fuel in these ovens; in some cases where the ovens are constructed with fire-grates and ash-pits, small coal may be used.

The mode of working is as follows. A charge of from 22 to 31 cwt. of pig lead is introduced into the furnace, and a dam is made across the furnace of rough oxide intermingled with lead obtained from the grinding and levigation of a previous charge. The temperature is so regulated as to melt the lead, which forms a pool behind the dam; the molten lead is agitated by means of a rabble and splashed over the furnace bottom. In this way the oxidation is promoted, and as the oxide is formed it is pushed toward the back of the furnace, the still unoxidised lead flowing to the front. The oxidation is promoted by adding a small quantity of 1 p.c. antimonial lead and when completed the charge is raked out into iron waggons, and allowed to cool It is next passed to the grinding mill, where it is ground between millstones with a regulated supply of water. The heavier particles of lead oxide and metallic lead which sink in the troughs leading to the settling cisterns are collected and used in the drossing oven to dam up the charge of lead. The finely ground massicot is carried by the stream of water into settling tanks where it subsides, and after the water has been run off, it is conveyed to the 'colouring' oven, spread out in furrows and ridges resembling a ploughed field, and heated at a carefully regulated temperature for some hours, until it has assumed the required shade. When hot, the red lead has a rich purple tint, which becomes bright red on cooling. The red lead is withdrawn from the ovens. and sieved or levigated.

In the manufacture of white lead by the stack process, a certain amount of the white lead (not more than 2 p.c. in a well-conducted operation) becomes stained. This 'off-colour' material is also used in making red lead and is worked either alone or mixed with ordinary materials.

A limited amount of red lead is also made by oxidation of lead (or litharge) with sodium nitrate. The nitrate is melted in iron pans, heated to 340°, and the calculated amount of lead in thin strips added. When the oxidation of the metal is complete, the mass is poured into warm water and the sodium nitrite recovered from the liquors, after these have been neutralised with sulphuric acid, by evaporation. The sodium nitrite is used in the dye industry for the purpose of diazotisation.

Orange lead or orange mineral is a variety of red lead produced by the calcination of white lead. Formerly, the froth from the white lead washing tanks was used for this purpose. The furnace-product is purified either by grinding finely and sifting, or it is water-ground, dried, and sifted. This variety is used for the production of paints, colours, printing inks, and enamels. The finest grades have a vivid orange tint. Orange lead differs from red lead, not only in colour, but also in bulkiness and in its behaviour towards linseed oil. It is much more bulky than red lead; the measures of equal weights of the two being as 7 : 5. This property is of great importance in the printing-ink trade.

When orange lead is mixed with linseed oil or varnish, the mixture remains soft on keeping, whereas red lead soon sets up with these media and the product cannot be thinned again. It is customary, therefore, when using red lead as a paint, to mix it shortly before use.

The cause of the variation in colour of the many grades of red and orange lead is not known. It has been found in laboratory experiments that small quantities (0·1 p.c.) of lead nitrate and caustic soda have a considerable effect, producing, in the first case, a pink colour, and, in the second, an intense red. When red lead is made by heating monoxide and peroxide of lead with caustic potash, the depth of colour depends on the concentration of the alkali. These facts, however, throw no light on the variations observed in large-scale operations. In these, the nature of the original materials, the control of furnacing temperature, and other factors, have a determining effect on the colour of the product.

Commercial varieties of red lead vary considerably in their content of active (peroxide) oxygen. The peroxide equivalent of this in the pure compound, Pb_3O_4 (*i.e.* approximately $2PbO.PbO_2$), is 34·9 p.c. A good average brand may contain 23–25 p.c.; extremes contain 5 and 34 p.c. For similar conditions in the colouring furnace, each kind of monoxide shows a maximum peroxidation, more or less definite, though the time required to establish this varies considerably. The past history of the monoxide affects the progress of oxidation. Thus both yellow and red litharge are roasted to red lead much more slowly after washing with water than after air-separation (O. W. Brown and A. R. Nees, J. Ind. Eng. Chem. 1916, 4, 867).

The effect of various factors on the rate of oxidation of litharge to red lead has been studied by J. Milbauer (Chem. Zeit. 1909, 33, 552, 950; 1910, 34, 139, 1341; 1915, 39, 858). It depends more on the source of the litharge than on the size of the particles, and is decreased by the addition of small quantities of nitric acid and ammonia, but increased by the nitrates of lead and sodium. Of the metals, silver facilitates oxidation at 300°, but its influence is not observable at a higher temperature; bismuth is inert and zinc and antimony act unfavourably. The velocity of oxidation also depends on the temperature and on the partial pressure of the oxygen.

Brown and Nees (*op. jam cit.*) state that the yellow and unfused varieties of litharge are more slowly oxidised than the red and fused forms. They have determined, under laboratory conditions, the optimum temperature of oxidation of various materials to red lead. This is 425°–430° for white lead, and 450°–470° for litharge and lead sponge (the latter obtained by electrolysing both acid and alkaline solutions of lead). According to their experiments, lead is not directly oxidised to red lead, but only *viâ* the monoxide.

These observers have also studied the microscopic structure of red lead and have determined the density of numerous specimens. The following is a brief abstract of the results. Red lead may be either crystalline or amorphous; no definite form can be made out for the crystalline varieties. The specific gravity varies from 8·32 to 9·16; it is lower the more nearly the composition approaches to Pb_3O_4, and its value depends on numerous factors, such as the temperature of oxidation, the length of time of heating, and the physical character of the original material. The apparent density depends mainly on the fineness of the particles, decreasing as the fineness increases up to a certain point.

When heated *in vacuô* to 530°, red lead is rapidly and completely converted into litharge. Heated in a closed space, between certain limits of temperature, the compound is dissociated into litharge (greenish-yellow in colour) and oxygen, and an equilibrium-system of two components in three phases is established. The dissociation-pressure of the compound is thus a function of the temperature. The pressure-temperature curve has been determined by Reinders and Hamburger (Zeitsch. anorg. Chem. 1914, 89, 71) between the temperatures 445° and 607°. It is smooth and gives no evidence of the formation of intermediate compounds or solid solutions. When the oxide has been purified by extraction with solutions of acetate or nitrate of lead, equilibrium is much more slowly attained than when the oxide is crude. (For the action of oxygen on litharge at high temperature and pressure, *see* p. 86.)

Several methods for the preparation of pure Pb_3O_4 have been given by Milbauer (Chem. Zeit. 1914, 38, 477, 559, 566, 587; *v.* also Dumas, Ann. Chim. 1832, 49, 398; and Levol, *ibid.* 1840, 75, 108). For example: (1) extraction with 10 p.c. solution of nitrate or acetate of lead, or with concentrated potash solution, of the oxide obtained by oxidising litharge at 470°, or that obtained by fusing litharge and potassium nitrate. (2) By heating lead peroxide PbO_2 with molten nitre at 470° and extracting the product with water. (3) By heating a mixture of monoxide and peroxide of lead ($3PbO : 2PbO_2$) with a solution of caustic potash containing 200 grams KOH dissolved in 100 c.c. water.

Red lead is regarded by some chemists, following Dumas (*op. cit.*), as lead orthoplumbate Pb_2PbO_4, and its formation as due to the combination of the basic monoxide PbO with the acidic dioxide PbO_2, which is the initial oxidation-product of the monoxide. Under particular conditions of oxidation the meta- or the pyroplumbate may be formed in a similar manner (*v.* p. 86). If a mixture of litharge and red lead of high active oxygen-content be compared with a red lead of lower active oxygen-content, but equal to that of the mixture, it will be observed that they differ, especially with respect to their behaviour towards linseed oil. Such facts have led to speculations on the chemical nature of red lead and its relationship to litharge. Mendeléeff's hypothesis of the polymerisation of lead monoxide (and other oxides) has been applied by Wade to the problem under consideration. It is assumed that the polymeride has some such formula as $Pb_{12}O_{12}$; that oxidation of litharge takes place gradually and uniformly through the mass and in such a way that successive stages, $Pb_{12}O_{13}$, $Pb_{12}O_{14}$, &c., are passed through. When the stage of oxidation represented by $Pb_{12}O_{16}(=4Pb_3O_4)$ is reached then pure red lead is the product.

Many of the present obscurities on this subject will probably vanish when knowledge of the homogeneity or otherwise of the grains of red lead has been acquired.

When heated, red lead assumes a darker shade of red, becoming violet and ultimately black; it regains its original tint on cooling. It is decomposed by nitric acid, lead nitrate and the puce-coloured peroxide PbO_2 being formed; when digested with nitric acid and a little sugar, the red lead is completely dissolved. Alcohol exerts a reducing action similar to that of sugar; the lead passes into solution as nitrate and the alcohol is oxidised to acetaldehyde. Red lead is used as a pigment, and in the manufacture of flint glass and optical glass. When used for the latter it must be free from iron, copper, antimony, metallic lead, and lead sulphate. It is also used as a cement in making steam joints, and in the manufacture of secondary batteries.

White lead, Céruse, Blanc de Plomb, Bleiweiss. The term ‘white lead’ has been used in England for at least three centuries to describe the mixture of basic carbonate (or carbonates) of lead and varying quantities of other lead compounds, which is produced by the action of air, moisture, carbon dioxide, and acetic acid upon lead. Within comparatively recent times, other methods of manufacturing white lead have been developed, but most of the output at the present day is still derived from the reaction of the above-named materials and by methods which are only variations of those used by the ancients.

The Stack process.—It is estimated that about 70 p.c. of the white lead produced in England is made by the stack process. This is developed from the old Dutch, and still earlier, processes, in which lead and pots of vinegar were embedded in fermenting horse dung and stable litter. The vinegar is replaced by acetic acid, prepared from pyroligneous acid and the dung by spent tan.

The substitution of spent tan for stable litter minimises the risk of discoloration of the white lead by sulphuretted hydrogen, but the fermentation is somewhat slower, and consequently the conversion of the ‘blue’ lead into white lead requires a greater length of time. The fermentation of the tan is thought to be due, at first, to bacterial action. In any case, heat is developed and the temperature may rise to 80°C., though 50°–60° is more usual. The carbon dioxide necessary for the process is produced in the fermentation, and the tan parts with much of its water.

The lead used for the manufacture of white lead should be pure, and the manufacturer usually refines it for the purpose. The presence of small amounts of copper or antimony tends to produce a white lead having a dull grey tint. A red or pink colour, at times observed in the white lead, has been attributed to the presence of a suboxide of lead by Bannow and Kraemer (Ber. 1872, 545; 1873, 21), an explanation admitted by Lorscheid, but according to Baker the coloration is caused by the presence of finely divided oxy-compounds of silver. The lead is cast into thin sheets of lattice work or gratings, so as to expose a large surface to reaction, by pouring molten lead on to a sloping grooved iron plate, from which, on solidifying, the crates, buckles, plates, straps, or wickets, as they are variously styled, are easily detached. Some is also cast in thin circular discs or stars. In some of the works in this country and in America, the ‘plates’ and ‘wickets’ are cast by machinery. The machine consists of an endless band of square plates of iron linked together, each plate being a mould, into which the lead is poured as the plates are slowly moved under the spout of the lead-pot. The castings are delivered at the end on a leather belt covered with plates of sheet iron to prevent the hot lead injuring the leather. This machine can make from 50–60 castings per minute.

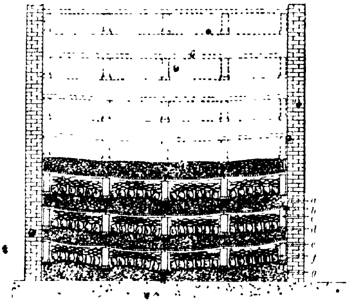

FIG. 28.—THE STACK PROCESS (diagrammatic)

a, Floor boards; *b*, Floor beams; *c*, Wood blocks keeping heights apart; *d*, Beams under wood blocks; *e*, Corroding strips of lead; *f*, Earthenware pots containing dilute acetic acid; *g*, Spent oak bark.

The corroding house or stacks is a brickwork chamber having an area of 12 feet by 20 feet, or 16 feet square, and a height of 25 feet. The front wall of the chamber is provided with an opening, 4 feet wide, running from the top to the bottom, which serves for the introduction of the materials used in the construction of the stack. As the building of the stack proceeds the opening is closed by boards fitting into slots, the top being, however, left open for the purpose of inspection. The stack is built up as follows: First, the floor of the chamber is

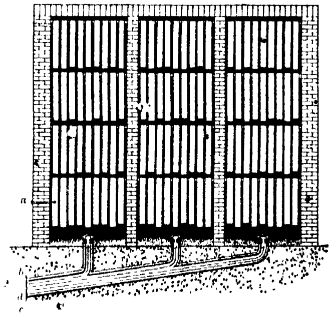

FIG. 29.—THE CHAMBER PROCESS (diagrammatic).

a, Straps of lead; *b*, Carbonic acid gas; *c*, Oxygen; *d*, Water vapour; *e*, Acetic acid vapour.

covered with a layer of ashes, upon which is spread spent tan, already in a state of fermentation; the thickness of this first bed of tan is 3 feet. The tan is beaten down and the surface levelled, and on the bed so formed earthenware pots, partially filled with a 2 or 3 p.c. solution of acetic acid, are placed side by side, leaving a space about 6 inches wide between the outside rows and the walls of the chamber. The pots ordinarily used are of two sizes; the larger ones are provided with a rim on the inside, on which discs of the metal rest. They are placed along the edges and support the wooden bearers which carry the flooring boards used to cover in the bed. Sometimes, pots of one size only are used, and the flooring boards are supported by blocks of wood. On the top of the earthenware pots are placed the crates of metallic lead, so as to form a layer of lead about 5 inches in depth; between the lead and the cover of flooring boards is left a space of from 6 to 8 inches. The space between the walls of the chamber and the pots is filled in with tan on all sides, the opening in front being closed by boards. On the bed so constructed another bed is built in exactly the same way, with the exception that in the construction of the upper beds the layer of tan is only about 1 foot in thickness. In this way the chambers are filled up to a height of 20 feet or more, and the topmost bed is covered with a layer of tan. In stacks of area 12 feet by 20 feet, 3 tons of lead are set per height and about 1000 pots of 5½ inches diameter, containing 200 gallons of dilute acetic acid. In stacks 28 feet by 14 feet, each height or set may contain as much as 7 tons of lead, the total for a stack of 12 heights being 84 tons

After the stack is built it is left to itself for about three months. It is then unloaded, the top covering of tan is removed, and the bark which is not mouldy is used to add to fresh tan in the construction of another stack. The 'corrosions' preserve the form of the castings of the metal, but are more bulky, and present a white opaque appearance. They vary in texture; the best corrosions are hard and porcellanous, and can be easily handled without crumbling, whilst the poorer are of a floury character and crumble easily when touched. In places the white lead is discoloured, owing to the tarry matter present in the acid used or to droppings of water from the tan. Before removal of the corrosions from the stack, each layer as it is exposed is thoroughly moistened with water to keep down the dust. It is usual to find the earthenware pots quite empty and dry, though a few may contain water; the pots are washed and drained, and used again. The pieces of white lead which fall on the bed of tan are picked up by hand, the surface of the bed is also raked and a further quantity of white lead is got from the tan by washing it on sieves in a stream of water.

The trays of corrosions taken from the stack are sunk in a cistern of water and the contents are directed by means of rakes between corrugated rollers running under a stream of water. After the blue lead has been separated, the white lead is crushed by passing through a pair of smooth rollers, made of gun-metal, and raked about over a perforated plate under a constant spray of water. The coarse white lead next passes to horizontal grinding stones, to which it is fed by a ladle or by an endless band. After passing through these stones, the white lead issues in the form of a thick white mud, and is again passed through other grinding stones until it has been reduced to a state of subdivision so fine that it is carried along by the stream of water to the settling tanks; the white lead which settles out in the troughs used to convey the water to the tanks is returned to the grinding stones. The grinding and levigating are conducted in such a way that the water may be used over again. Before discharging the water, sodium carbonate solution is added to precipitate the lead, present as soluble acetate. Sometimes the sodium carbonate is added during the grinding process and the resulting sodium acetate eliminated in the settling tubs and filter presses. It is essential that white lead should be free from lead acetate.

In the tanks the white lead gradually settles and forms a thick white paste, from which the water is siphoned off, and when the mud has attained a sufficient consistence it is ladled out into the dishes used for drying it. The dishes are shallow clay saucers, 12 inches diameter and 3 inches deep, and made of clay similar to that employed in making flower pots. The dishes are stacked in drying stoves upon shelves made of iron bars, the stoves are heated by iron pipes made to circulate round the floor of the stove, and connected with a fireplace outside the stove, the products of combustion from the fire passing through the pipes. In this way the pulp, which contains 25-30 p.c. of water, is gradually dried; the temperature of the stoves should not rise above 180°F. (62°C.). Drying is also performed in steam-heated copper pans, and under reduced pressure. The white lead when dry is packed in casks or ground and mixed with oil to form a paint. Boiled linseed oil is used for this purpose, and the 'paste' produced contains 6-9 p.c. of oil. During the grinding, some manufacturers add a small quantity of a blue colouring matter such as Prussian blue or indigo to the white lead to modify the somewhat yellowish tint due to the stains from the bark.

To obviate the dangers attending the drying of the pulp, the method patented by Ismay (Eng Pat. 23969, 1895), and known as 'pulping,' has been adopted with considerable success. In this process, the white lead pulp from the filter presses is mixed with oil and thoroughly agitated in a pug-mill, with the result that the greater portion of the water is displaced by the oil: the last portion of water is driven off by using a pug-mill, provided with a heating jacket, in which the mixture is heated to a definite and regulated temperature in a partial vacuum. This method contributes a considerable hygienic advance.

One of the great disadvantages of the stack process is the lack of control of the fermentation of the tan. In practice, great attention is paid to this subject, the tan being kept under close observation during the building of the stack Any irregularities in action, arising during the corrosion, naturally affect the development of heat, which influences the evaporation of the acetic acid, and the generation of carbon dioxide.

The Chamber Process has been developed chiefly in Germany and is there used extensively. In this country, Cookson's Chamber Process, modelled on the German, is in operation on the Tyne. The outstanding differences between the chamber and the stack processes are that tan *is dispensed with as a source of heat and carbon dioxide; all the necessary materials are passed* into the corroding chambers in regulated quantities and very thorough control of temperature and other factors is possible.

The corroding chambers are built of brick and are about 21 feet high and 20-25 feet square. The gases are generated beneath the chambers and enter them through pipes in the floor; at the top of the chambers there are openings for ventilation which can be closed, if necessary, by wooden plugs. Air is admitted through the sides of the chamber, near the base.

The refined lead for corrosion is cast into straps, without perforations, and thinner than those used in the stack process: these are slung over sticks which are carried on arches. The total weight of lead set in an average chamber is 45-55 tons. Carbon dioxide is generated by burning weighed quantities of coke, of known composition, the weight of carbon burnt being only slightly in excess of the amount eventually contained in the white lead, reckoning on an average corrosion. Water and acetic acid are evaporated in fire-heated copper pots, somewhat more acid being used than in the stack process. The temperature is 60°-70°C., and the heat is supplied by the hot gases, supplemented to some extent by the heat of chemical action.

The time of corrosion is from 42 to 60 days, and the proportion of the lead corroded is greater than in the stack process; it depends on the size and weight of the straps and on the quantity of lead set in each height. Before stripping, the chambers are thoroughly drenched with water by means of special sprays placed in the ventilating holes. The corrosions are taken to the grinding mills and are treated in the same manner as those produced in the stack process.

The following analyses of chamber gases are averages, over a long period, for two chambers:

	1	2
Oxygen . .	14·0	15·4
Carbon dioxide .	0·67	0·24

These figures are instructive as showing the extent to which atmospheric oxygen is absorbed in the process. This point may be emphasised by a simple calculation. Suppose that 50 tons of lead are set in a chamber 25 feet cube and that 60 p.c. is corroded in 60 days. The average temperature being 60°C.; then the weight of atmospheric oxygen absorbed is 2·3 tons, which occupies 62,300 cubic feet at 60°. The absorption of oxygen is thus, in round numbers, 1000 cubic feet a day, which is equivalent to one-third the air-contents of the chamber. The atmosphere of the chambers is saturated with water vapour. The pressure of this at 60° is 150 mm., so that the gases contain 20 p.c. of water vapour

One great merit of the chamber process lies in the control which can be exercised over the temperature and the composition of the reacting gases. The spaciousness of the chambers is possibly also an advantage, since it favours the convection and diffusion of the gases and the establishment of uniform composition. The absence of dirty bark and coloured drippings results in the white lead being cleaner than that *produced in the stacks. Comparison of the two products shows the stack white lead to* have a pronounced grey colour, whereas the chamber product is pure white. By selection of the composition of the reacting gases, a corroder can naturally cause the composition of the white lead to vary within wide limits; actually, he works for a product of uniform composition. An average analysis shows: PbO = 86·4; CO_2 = 11·3; H_2O = 2·3 p.c., which corresponds closely with the formula $3PbO.2CO_2.H_2O$ (calculated: PbO = 86·3; CO_2 = 11·4; H_2O = 2·3) For similar grades of fineness, the amount of 'coarse' (normal) carbonate, insoluble in dilute acetic acid of the same strength is only 0·1 to 0·3 p.c. for the chamber white lead, but it varies from 6 to 20 p.c. for the stack white lead. The following figures, which are averages over a long period, illustrate this difference of carbonation in the two processes:

Molecular ratios	Chamber white lead	Stack white lead	
		Ordinary run	Short run
	x	x	x
xPbCO$_3$·Pb(OH)$_2$	1·88 to 2·56	2·22 to 2·72	2·07

The greater extent of carbonation of the stack product is thus clearly shown. When the stack is worked on a short run (about half the normal) the carbonation is not so pronounced and the white lead approximates in character and composition to the chamber product.

THE CHEMISTRY OF WHITE LEAD.

Though so much has been written on this subject, it cannot be said that our knowledge of the many changes which take place in the conversion of lead into white lead by the stack or chamber process is in a satisfactory condition, and the general tendency to speak of white lead as a compound, instead of a commercial preparation, has given a spurious air of simplicity to what is, in reality, a very complicated problem.

All are agreed that corrosions are not uniform in composition: they vary from layer to layer and contain one or more basic carbonates of lead and, in addition, acetate and normal carbonate of lead and, possibly, lead hydroxide. The futility of calculating formulæ from the analyses of selected pieces of corrosions is at once apparent.

White lead itself is a more uniform product and is probably simpler from a chemical point of view Most of the lead acetate, normally present in the corrosions to the extent of 2 p.c., has either been washed out or precipitated as basic carbonate, either by the carbon dioxide of the air or by the addition of sodium carbonate, and any lead hydroxide which may have been present originally has likewise been converted into basic carbonate during the washing process; and though normal carbonate of lead is probably present in all samples, the quantity of it may be small. The question then arises whether the bulk of the finished white lead can be regarded as consisting of one compound, and, if so, what formula are we to assign to it?

The ability of manufacturers to turn out white lead of fairly constant composition, in tolerable agreement with the formula

$$2PbCO_3,Pb(OH)_2$$

has naturally led most writers on the subject to conclude that this compound is the basis, as it were, of white lead, though it would be legitimate to infer that a complex mixture, say, of normal and basic carbonates of lead was in all cases produced and that uniformity in composition was only a measure of the control of conditions exercised during the manufacturing process.

The difficulty of deciding between these views arises from the poor characterisation of the material and the consequent lack of satisfactory criteria for the existence of any definite compounds in white lead, except the crystalline normal carbonate, which is often only a subsidiary constituent. As, however, a definite basic carbonate of the composition

$$2PbCO_3 Pb(OH)_2$$

does exist (Hawley, J. Phys. Chem. 1906, 10, 654), and as it can be prepared by similar methods and resembles white lead in properties, it may be assumed that this compound is a constituent, and possibly an important one, of a good white lead, and the question of the presence of other basic carbonates in white lead may be left open. The old idea, which still crops up on occasion, that white lead is a mixture of hydroxide and carbonate of lead is erroneous, and it might be well to minimise the possibility of this error by writing the formula of the basic carbonate on an analytical basis as $3PbO{\cdot}2CO_2{\cdot}H_2O$. This would have the further advantage of discouraging names with a constitutional connotation, and it might end the absurdity of representing white lead with a structural formula. The statement, so often met with, that a white lead has the 'theoretical composition' must be read in the light of the above qualifications.

The explanation of the corrosion process put forward by Liebig and Hochstetter (1837) is generally accepted, differences of opinion arising over what are, relatively speaking, minor points. The reactions postulated are:

1. Oxidation of lead, in presence of water, by atmospheric oxygen and conversion of lead hydroxide into lead acetate by means of acetic acid;

2. Formation of basic lead acetate by reaction between lead hydroxide and (normal) lead acetate;

3. Double decomposition of basic acetate of lead and carbonic acid, with production of basic carbonate of lead and regeneration of acetic acid. The acetic acid is immediately converted into its lead salt, during active corrosion, and this by combining with more lead hydroxide sets up afresh this cycle of changes. Viewed otherwise, one may regard the normal lead acetate solution as the solvent in which lead hydroxide, produced by direct oxidation of the metal, is continuously dissolving, and from which it is being continuously precipitated as basic carbonate of lead by the carbonic acid.

The assumption of this succession of reactions, though satisfactory enough as concerns the main issue, yet fails to represent the complexity of the corroding-house process, for clearly there must be ceaseless competition of the various bases present for the two acids. Full discussion of this problem would be out of place here, but brief mention may be made of some effects which would follow disturbance of what might be called the normal process of corrosion.

Excess of acetic acid would tend to form normal lead acetate, both from the basic acetate and the basic carbonate; if this were followed by excess of carbonic acid, the normal lead carbonate would be precipitated. The disappearance of the core of blue lead from a corrosion, owing to the complete oxidation of the metal, would stop the feed of lead hydroxide into the reacting system with the result that normal lead acetate would be produced and this again would yield normal carbonate by reaction with carbon dioxide. Finally, excess of carbon dioxide converts the basic carbonate of lead itself slowly into the normal carbonate.

The general result of these changes is thus to increase the amount of normal carbonate of lead in the corrosions, and the relative stability of that compound towards both acetic and carbonic acids tends to its preservation. Thus by the assumption of these simple and probable reactions one can explain the degradation of white lead, that is, the production from the basic carbonate of a preparation rich in coarse carbonate and not conforming to the 'theoretical composition.'

Other methods of making White Lead.—A great many methods have been suggested and put into operation; most of these are now only of historical interest, and none has attained technical importance comparable with the stack and chamber processes. Some of the methods are based on the old process, that is, they use lead acetate as intermediary; examples of these are the French or Clichy, and the Carter processes.

In the French process, basic lead acetate is produced by digesting litharge with acetic acid; or, in a modified form of the process, by oxidising lead powder or ribbon with air in presence of lead acetate solution. The solution is then clarified by settling and carbonated, the white lead separated from the lead acetate solution, and the latter returned to the process for conversion into basic acetate.

The Carter process, used successfully in America, shortens the time of corrosion to 12 days by operating on finely divided lead which is kept in constant agitation. The granulation of the metal is brought about by allowing a jet of high-pressure steam to impinge on a stream of molten lead. This metal is then placed in large wooden drums, which revolve slowly, and is sprayed at intervals with water and acetic acid. Flue gases, containing 10 p.c. of carbon dioxide, purified by bog ore, are passed through. The unchanged lead is constantly exposed by attrition. The product is levigated in the usual manner.

Basic salts other than the acetate have been suggested or employed in some processes. In one of these the basic nitrate is used; in Milner's process, the basic chloride. The latter compound is prepared from litharge, sodium chloride, and water, and the resulting sludge of basic chloride and caustic soda is carbonated until the liquor is free from alkali. White lead and sodium chloride are thus produced and the salt is removed by washing.

The Bischof process, worked by the Brimsdown Lead Co. in Middlesex, differs, especially in the initial stages, from any of the above. Flake litharge is ground finely and reduced by water-gas to the black sub-oxide of lead, Pb_2O (*v.* p. 85). This is transferred to steel pans, moistened with a limited quantity of water and well stirred by revolving blades. Hydration and oxidation take place. The product is mixed into a paste with water and carbonated, after addition of a little acetic acid White lead is formed, presumably with simultaneous generation of lead acetate, which forms basic acetate with the hydroxide and thus plays the part of catalyst. The whole operation lasts about two days.

One of the most interesting methods for making white lead is used in America, and is called the Rowley or Mild process. Acetic acid and its salts, as well as salts of other acids (hydrochloric, nitric, &c.) are dispensed with altogether, and the reacting substances are the simplest possible, viz. lead, oxygen, water, and carbon dioxide. The lead, which need not be of a high degree of purity, is finely granulated as in the Carter process, and the black, metallic sludge is agitated 24 36 hours in presence of air, 80-90 p.c. of the metal being thereby oxidised and converted into 'hydrated lead.' This is elutriated and then treated for 36 hours in rotary carbonators with flue gases containing 18 p c. of carbon dioxide, whereby white lead is produced. The product requires no washing or grinding and is said to have the 'theoretical' composition

Properties of White Lead.—Commercial white leads are not of uniform composition and they vary a good deal with respect to those important properties upon which their use as a pigment depends. Such variations are, however, not uniquely connected with composition, they depend also on the fineness and uniformity of grain, on the presence of normal lead carbonate and, possibly, on many other conditions. A sample of 'theoretical' composition is not necessarily the best in actual practice. It seems to be admitted however, that the carbon dioxide should fall between 11 and 13 p.c., otherwise the white lead is defective as a pigment.

So far as it is possible to generalise on a product which is not uniform, it may be stated that white lead is amorphous, of sp.gr. 6·45, and it loses water completely at 150° without parting with carbon dioxide. The grain depends on the method of preparation and the grinding. The grains of mild white lead are uniform in size, whereas those from material prepared by the stack process vary in diameter from 0·00002 to 0·00026 inch. Probably most samples contain crystalline normal lead carbonate, some of which is left as residue when the white lead reacts with dilute acetic acid. The analysis of such a residue from the chamber lead shows it to consist essentially of lead carbonate:

$PbCO_3$ . .	97·81 p.c.
$PbSO_4$ . .	0·84 ,,
$CaCO_3$ $FeCO_3$ . .	0·97 ,,
SiO_2 . . .	0 34 ,,
Organic matter .	0 11 ,,
	100·07 ,,

It is generally admitted that this crystalline carbonate is useless as a pigment.

Much controversy has arisen with regard to the changes which take place when white lead is ground with linseed oil, the main issue being whether hydrolysis of the oil takes place or not. If any particular preparation of white lead contained lead hydroxide, it would be natural to expect hydrolysis or saponification; but if it consisted of a mixture of normal and basic carbonates of lead, there would be no reason *a priori* to anticipate such a reaction. The experimental work of Davis and Klein (J. Soc. Chem Ind. 1907, 26) has shown that lead soaps are indeed formed from white lead and linseed oil, and that some of these are insoluble and others soluble in ether, but these authors ascribe their formation entirely to reaction of the white lead with the free fatty acids present in the oil. The evidence is against saponification; in any case, very small amounts of lead soaps are formed.

Two objections to the use of white lead as paint are that it is discoloured by hydrogen sulphide, owing to the formation of black lead sulphide, and that it suffers from 'chalking' or 'flouring,' a kind of granulation. The defect last mentioned sometimes becomes evident a few months after the application of the paint. Its cause is obscure and has been variously traced to the presence of fatty acids in the oil, over-heating during grinding, and the presence of lead acetate in the white lead (*see* Holley, Zinc and Lead Pigments).

Substitutes for White Lead.—'Genuine' brands of white lead are pure in England; adulteration of white lead with barium sulphate is recognised both by manufacturers and merchants, and such mixtures are known as 'reduced' white leads. Of substitutes proper, mention may be made of the basic chloride and sulphate of lead.

The basic chloride is now of historical interest only, its manufacture having been patented by Pattinson in 1849 and abandoned after some years' trial. It was prepared from galena by converting this into the chloride with hydrochloric acid and precipitating the solution of lead chloride with half its equivalent of lime. The basic chloride has the same composition as the mineral laurionite, $PbO, PbCl_2, H_2O$.

Bartlett's 'sublimed white lead' is a mixture of basic sulphate of lead and zinc oxide. It is prepared from high-grade galena concentrates, containing some blende, by heating these in a modified form of blast-furnace and directing a powerful blast of hot air upon the mineral. Galena is readily volatilised at a high temperature, and the vapour on oxidation yields a dense fume which, after passing through coolers and dust-condensing flues, is filtered through bags. When conditions are properly controlled, the product is fairly uniform in composition, the range of variation of the chief constituents being:

Lead sulphate	75–80 p.c.
Lead oxide	14–20 „
Zinc oxide	5–6 „

The lead is stated to be present as the basic sulphate $2PbSO_4 \cdot PbO$, or $3PbO,2SO_3$. The product is a white, fine-grained, amorphous powder, having the covering power of white lead. It is less susceptible than white lead to discoloration by hydrogen sulphide and its specific gravity is slightly lower, viz. 6·2. It is especially useful in making mixed paints.

Lead Poisoning.

The compounds of lead, more especially the soluble ones, are strongly poisonous, and since the poison is cumulative, it produces serious results if taken into the system even in minute quantities for any length of time. One way in which lead is introduced into the system is by the use of drinking waters, some of which easily attack the lead of the pipes used for conveying the water. Again, the workpeople engaged in the manufacture of lead and lead compounds, and those who use them in such trades and industries as painting, printing, plumbing, file-cutting, enamelling, the manufacture of accumulators, china and earthenware, are liable to suffer from lead poisoning. The symptoms are pain in the abdomen, constipation, loss of appetite, thirst, a nervous prostration known as lead palsy, epileptic fits, and total paralysis. One of the signs of chronic lead poisoning is a blue line at the edges of the gums, due to the deposition of lead sulphide. This line is, however, not diagnostic; it is a secondary effect arising from a septic condition of the mouth and seldom occurs when the teeth are sound and the gums clean.

Susceptibility towards lead poisoning depends on many things. Women are more susceptible than men, and the underfed are naturally more prone to attack than the well-nourished. Anaemia is one of the chief predisposing causes. Most people become tolerant of the poison to some degree, a certain balance being struck between absorption and secretion. This balance may be upset, with serious results, by the onset of disease or by a sudden increase in absorption.

In cases of industrial poisoning, it would appear that dust is the chief cause of infection, gastro-intestinal and cutaneous absorption being quite of secondary importance. Hence, the use of efficient exhaust ventilation in dusty operations, such as the drying of white lead, has been attended by a very great decrease in the number of cases of poisoning, the official figures for English white lead workers being 399 for the year 1899 and 23 for the year 1913. In 1918 not a single case was recorded. The wet-pulping process is a great improvement in this connection, and other important factors are selection, education and medical inspection of the workfolk, provision of respirators, overalls, and simple medicines, and general attention to hygiene and bodily cleanliness.

A portion of the lead taken into the system is excreted by the kidneys, and in cases of chronic lead poisoning it is stated that the administration of potassium iodide aids in the elimination of lead from the system. The mode in which the compounds of this metal are distributed in the different organs of the body is illustrated by the following results of an examination made by Drs. Bedson and Drummond and Sir Thomas Oliver in the case of three workpeople who succumbed to the influence of this form of poisoning:—

Description of organ, &c.	Lead found expressed as metallic lead in parts per million			Lead in grains calculated on total weight of organ		
	I	II	III	I.	II.	III.
Large intestine	14·6	37·7	—	—	—	—
Small intestine	9·2	—	—	—	—	—
Muscle	3·1	—	—	—	—	—
Lung	2·2	7·6	—	—	—	—
Heart	6·7	4·12	5·0	0·0243	0·0189	0·01[illegible]4
Mamma	4·8	—	—	—	—	—
Kidney	15·5	10	13·3	0·027	0·0229	0·0261
Spleen	14·7	12	39·0	0·0193	0·0341	0·0853
Liver	47·7	37·8	41·6	0·918	1·000	0·728
Cerebellum and pons	36·9	—	—	—	—	—
Grey matter of basal ganglia	53	—	—	—	—	—
Brain, grey matter of cortex	40·9	—	—	—	—	—
Brain, white substance	18·9	—	—	—	—	—
Spinal cord	—	1·16	—	—	—	—
Brain	—	9·8	21·6	0·688	—	—
Cerebellum	—	24·8	8·59	—	—	—
Pons	—	22·6	—	—	—	—
Brain and cerebellum	—	—	—	—	0·779	0·634

Other Compounds of Lead.

Oxides. Besides the wto oxides described above several others exist.

Lead suboxide Pb_2O is formed when lead oxalate is heated in the absence of air at a temperature below 300°; or when lead oxide is reduced with carbon monoxide at 300° (Brislee, Chem. Soc. Trans. 1906, 154). It is a black velvety powder of sp.gr. 8·342 at 18°, which is readily decomposed into the metal and the monoxide when heated or when treated with caustic soda. Dilute acids liberate lead and yield the salts derived from the monoxide.

Lead sesquioxide Pb_2O_3 is generally considered to be either lead metaplumbate $Pb(PbO_3)$ or a compound of the mono- and di- oxides $PbO{\cdot}PbO_2$, into which it is decomposed by acids. It is a yellowish-red powder, formed by adding a solution of sodium hypochlorite to a cold potash solution of lead oxide, or by precipitating an acetic acid solution of red lead with dilute ammonia.

By heating monoxide, peroxide, or carbonate of lead to 400°–450° in oxygen, at a pressure of 100 atmospheres, a dark brown oxide is formed of the composition Pb_5O_8. This may be regarded as lead pyroplumbate $Pb_2(Pb_3O_8)$, and the relation of pyro- to ortho-plumbic acid may be represented:

$$3H_4PbO_4 - 4H_2O = H_4Pb_3O_8$$

(F. Fischer and H. Ploetze, Zeitsch. anorg. Chem. 1912, 75, 19).

Lead peroxide (*Lead dioxide* or *Puce-coloured oxide of lead*) PbO_2 is found native in *plattnerite*, which crystallises in black hexagonal prisms of sp.gr. 9·4. It may be prepared by the action of nitric acid on red lead, by the action of chlorine on a lead salt in the presence of an alkali, or better by the action of bleaching powder on lead chloride (Fehrmann, J. Soc. Chem. Ind. 1882, 407). A lead peroxide suitable to the requirements of the aniline manufacturer may be obtained by adding the required amount of lead oxide to molten caustic soda at the highest possible temperature, with constant stirring, and then sufficient sodium nitrate for oxidation. The mass is then extracted with hot water, washed, and dried (Minor, J. Soc. Chem. Ind. 1894, 940).

Normal or basic lead sulphate may be converted into lead peroxide, by mixing it with magnesia, suspending the mixture in water and passing in chlorine. It is purified by treatment with boiling 10 p.c. caustic soda, then with hot nitric acid. The yield is almost theoretical, and the oxide is of 97 p.c. purity, containing only traces of chlorine (Friedrich, Mallet, and Guye, Monit. Scient. 1906, 20, 514).

The reaction may be represented thus:

$$PbSO_4 + MgO = MgSO_4 + PbO;$$
$$PbO + MgO + Cl_2 = PbO_2 + MgCl_2$$

Lead peroxide may also be obtained electrolytically when water containing less than 1 p.c. of acid, alkali, or salt is electrolysed, using a lead sulphide anode: $PbS + H_2O + 5O = PbO_2 + H_2SO_4$ (D. R. P 162107; *see* also D. R. P. 124512; Eng. Pat 12186, 1901; J. Soc. Chem. Ind. 1897, 743; *ibid.* 1902, 620; Hollard, Compt. rend. 1903, 136, 229). When a strongly alkaline plumbite is oxidised with potassium persulphate, an active oxide, containing 93 p.c., PbO_2, is formed (Panopolus, Chem. Zeit. 1916, 40, 339). Pure lead peroxide is obtained by oxidising a solution of lead nitrate in caustic soda (20 p.c.) with hydrogen peroxide (Zotier, Bull. Soc. chim. 1917, 21, 244)). (For other methods of preparing the peroxide *see* Eng. Pats. 11962, 1889; 6954, 1903; Warren, Chem. News, 1896, 144.) Lead peroxide is a dark brown, almost black, powder of sp.gr. 8·9–9·2, which is said to keep best when moist (Fehrmann, *l.c.*). On exposure to sunlight it forms red lead and dissociates on heating into lead monoxide and oxygen; there is no evidence of the formation of red lead or any other oxide but litharge in this process (Reinders and Hamburger, Zeitsch. anorg. Chem 1914, 89, 71). It has a powerful oxidising action, taking fire when triturated with sulphur, and igniting sulphuretted hydrogen when the latter is passed over it, the heat of this reaction being such that explosives like guncotton or picrate can be fired and metallic powders ignited by its aid (Vanino and Hauser, Ber. 1900, 33, 625). A large number of organic compounds when triturated with it also cause an evolution of heat and light. It decomposes or oxidises some mineral acids, forming the corresponding lead salt often with violent evolution of gas. Lead peroxide combines readily with sulphur dioxide, forming lead sulphate. It can be used for separating sulphur dioxide from carbon dioxide and is often employed for this purpose and as an oxidising agent in the analysis of organic compounds containing sulphur; it has also been used in inorganic analysis for the removal of excess of sulphuretted hydrogen or ammonium sulphide (Bogdan, Bull. Soc. chim. 1903, 29, 594). Lead peroxide has been used as a mordant and also for the precipitation of other oxides on the fibre (Bonnet, Bull. Soc. Ind Mulhouse, 1894, 69; Compt. rend. 1893, 117, 518). It has also been used in the voltaic battery and in electrical and metallurgical operations (Eng Pat. 16608, 1886; J. Soc. Chem. Ind. 1888, 37). Lead peroxide acts as a weak basic oxide, forming unstable quadrivalent lead salts and also as an acid-forming oxide yielding the *plumbates*. *Orthoplumbates* of the composition M_4PbO_4 and *metaplumbates* $M_2PbO_3,3H_2O$ or $M_2Pb(OH)_6$ have been prepared (Fremy, Ann. Chim. Phys. 1844, [iii.] 12, 490; Grützner and Höhnel, Arch. Pharm. 1895, 233, 512; Bellucci and Parravano, Gazz. chim. ital. 1905, 35, ii. 500).

The orthoplumbates evolve oxygen when strongly heated, and on this fact has been based a method of obtaining oxygen from air on a large scale; the calcium salt has also been used as an oxidising agent (Kassner, Arch. Pharm. 1890, 228, 109; *ibid.* 1894, 232, 375; *ibid.* 1895, 233, 501).

When calcium meta- or orthoplumbate is heated in a current of air at 200°–280°, *calcium perplumbate* $CaPb_2O_6$ is formed (Kassner, Arch. Pharm. 1899, 237, 409; *ibid.* 1900, 238, 449).

When potassium plumbate is treated with water at the ordinary temperature it is completely hydrolysed, and *plumbic acid* H_2PbO_3 remains in solution in the colloidal state (Bellucci and Parravano, Atti R. Accad. Lincei, 1906, v. 15, ii 542, 631; Parravano and Calcagni, Gazz. chim. ital. 1907, 37, ii. 264).

Lead hydroxide $Pb(OH)_2$ is formed when potassium nitrate is electrolysed, a lead anode being used (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 436). It may also be prepared by heating lead carbonate with water or steam (Eng. Pat. 9521, 1893), or by treating lead sulphate with excess of alkali hydroxide (U. S. Pat. 787451, 1905; *see* also U. S. Pat 808141, 1905; Fr. Pat. 401473, 1909). It acts as a very weak acid (Hantzsch, Zeitsch. anorg. Chem. 1902, 30, 308; Rubenbauer, *ibid.* 331), and has also been obtained in a colloidal form (Sziland, J. Chim. Phys. 1907, 5, 636). The action of lead hydroxide on sugars is similar to that of the alkali hydroxides, inducing molecular rearrangement (Lobry de Bruyn and Eckenstein, Rec. trav. chim. 1896, 15, 92; U. S. Pat. 726130, 1903).

Two *hydrated lead monoxides* are known, $2PbO \cdot H_2O$ or $PbO \cdot Pb(OH)_2$ and $3PbO \cdot H_2O$ or $2PbO \cdot Pb(OH)_2$. The former is obtained as a white powder by the action of air and water on the metal or by precipitating a lead salt with a small quantity of alkali or ammonia. It may also be obtained in hexagonal crystals by exposing a cold solution of lead monoxide in caustic potash to the air (Ludeking, Amer. Chem. J. 13, 20). The latter basic hydroxide has been prepared by precipitating basic lead acetate with ammonia (Payen, Ann. Chim. 1866, [iv.] 8, 302). It forms a white crystalline powder or glittering octahedra, according to the method of preparation. The accuracy of these formulæ for the hydrated lead monoxides, as well as for lead hydroxide itself, has been recently called into question (S Glasstone, Chem. Soc. Trans. 1922, 58).

Halogen compounds of lead. The three subhalides have been prepared by heating plumbous oxide in the vapour of the alkyl halides; the chloride at 311°, the bromide at 261°, the iodide at 262°. The first two are grey and the iodide is a bright yellow powder. They are all difficult to prepare, requiring definite conditions and the maintenance of temperature and pressure within narrow limits. They are oxidised by air, especially when moist, and are decomposed into metal and normal halide when heated above their temperature of formation or when brought into contact with acids They are much less soluble than the normal halides, the solubility-data in milli-equivalents per litre at 25° being: PbCl, 2·2; PbBr, 0·4; PbI, 0·17 (H. G Denham, Journ. Chem. Soc. 1917, 111, 29; 1918, 113, 249).

The normal halides. *Lead chloride* (*horn lead, plumbum corneum*) $PbCl_2$ occurs native in the craters of volcanoes as the mineral *cotunnite*, and may be prepared readily by treating the oxide or carbonate with hydrochloric acid or by precipitating a fairly concentrated solution of a lead salt with a soluble chloride. On a large scale it may be prepared by heating litharge with a slight excess of hydrochloric acid at 200° and 25 atmos. pressure, in an autoclave lined with an acid-resisting material (Eng. Pat. 12953, 1895; *see* also Eng. Pats. 16213, 1889; 8914, 1895; J. Soc. Chem. Ind. 1890, 941; *ibid.* 1895, 873; *ibid* 1896, 357). In a colloidal form it can be obtained by mixing together lead acetate or the lead salt of any other organic acid with an alkali, or alkali earth chloride (van de Velde, Chem. Zeit. 17, 1908).

Lead chloride forms a white crystalline precipitate or white silky rhombic needles of sp.gr. 5·8. When heated in absence of air it melts at 495°, and boils at 945° at 754 mm. The heat of vaporisation at m.p. is 40,600 cals. It is less soluble in dilute hydrochloric acid and in solutions of chlorides than in water, but dissolves more readily in concentrated hydrochloric acid (André, Compt. rend. 1883, 97, 1302; Lichy, J. Amer. Chem. Soc. 1903, 25, 469). The solubility is at a minimum when there is 10 p.c. of hydrochloric acid in the solution. It dissolves in alkali acetates and in thiosulphates, forming a lead thiochloride $Pb_4S_6Cl_2$ (Hofmann and Wolff. Ber. 1904, 37, 249).

Lead chloride forms double salts with ammonium and other metallic chlorides (André, Compt. rend. 1883, 96. 435; Lorenz and Ruckstuhl, Zeitsch. anorg. Chem. 1906, 51, 71; Ephraim and Barteczko, *ibid.* 1909, 61, 245; Foote and Levy, Amer. Chem J. 1907, 37, 119; J. Soc. Chem. Ind. 1909, 707).

A large number of lead oxychlorides are known. The compound $PbCl_2,PbO$ occurs in nature as the mineral *matlockite*; it forms long thin colourless needles, decomposing at 524° into a mixture of $PbCl_2.2PbO$ and PbO, which fuses completely at 615°. The hydrated oxychloride of similar composition constitutes the mineral *laurionite* $PbCl_2,PbO.H_2O$. $PbCl_2,2PbO$ occurs as *mendipite*, and forms long glistening needles, m.p. 693°. The compound $PbCl_2,4PbO$ has m p. 711°, and forms glistening lamellar crystals, which give an intense yellow powder (Ruer, Zeitsch. anorg. Chem. 1906, 49, 365; *see* also Strömholm, *ibid.* 1904, 38, 429; Berl and Austerweil, Zeitsch. Elektrochem. 1907, 13, 165). The compound known as *Cassel yellow* has the approximate composition $PbCl_2,7PbO$, together with a little lead, and is usually prepared by fusing together 1 part ammonium chloride, and about 10 parts massicot, white lead, or minium. It is used as a pigment.

Lead tetrachloride $PbCl_4$ may be formed by passing chlorine into lead chloride, suspended in strong hydrochloric acid at 10°-15°. On adding ammonium chloride, *ammonium plumbichloride* $(NH_4)_2PbCl_6$ separates (Hutchinson and Pollard, Chem. Soc. Trans 1899, 212; Seyewetz and Trawitz, Compt. rend. 1903, 136, 686; Bull. Soc. chim. [iii.] 29, 261; Elbs and Nubling. Zeitsch. Elektrochem. 1903, 9, 776).

When this ammonium compound is added little by little to ice-cold concentrated sulphuric acid, lead tetrachloride separates as a yellow highly refractive oily liquid, which fumes in air, smells like hypochlorous acid, and induces a sweet taste in the mouth. It has sp.gr. 3·183, is stable under sulphuric acid, but is liable to explode, especially when heated, forming chlorine and lead chloride. It solidifies at --15° to a transparent yellow crystalline mass. With hydrochloric acid it forms a crystalline compound H_2PbCl_6, which dissolves on further addition of acid, and is decomposed by water into lead dioxide and hydrochloric acid (Friedrich, Monatsh. 1893, 14, 505; *see* also Ber. 1893, 26, 1434; de Coninck, Bull. Assoc. belge Chim. 1902, 16, 94). Many salts of this chlorplumbic acid have been prepared, some, like the potassium salt K_2PbCl_6, in crystalline form. A great number of salts derived from organic bases are also known. When these are well crystallised, regular and rhombic forms predominate The chlorplumbates of pyridine and quinoline are stable. Solutions of these organic derivatives, when treated with ammonia, yield precipitates of lead peroxide; hydrogen peroxide reduces them to plumbous salts. (A. Gutbier and M. Wissmüller, J pr. Chem. 1914, 90, 491).

Lead chlorite, *chlorate*, and *perchlorate* are also known.

Lead bromide $PbBr_2$ is obtained by treating lead oxide with aqueous hydrobromic acid or by precipitating a lead salt with a soluble bromide. It forms white shining needles, which darken when exposed to sunlight (Norris, Amer. Chem. J. 1895, 17, 189); sp.gr 6·6. It resembles the chloride in properties.

It forms double bromides and oxybromides.

Lead iodide PbI_2 is formed by dissolving lead in hydriodic acid or by precipitating a solution of a lead salt with a soluble iodide. It forms yellow crystals of sp gr. 6·1, which on heating become yellowish-red, bright red, and finally brownish-black. It also forms double salts and basic salts.

The chloride, bromide and iodide yield double salts with pyridine and quinoline (Elbs and Nübling, *l.c.*).

A number of mixed halogen compounds are known (Thomas, Compt. rend 1898, 126, 1349; *ibid.* 1899, 128, 1234, 1329; Fonzes-Diacon, Bull. Soc. chim. 1897, [iii.] 17, 346; Hertz and Bogg, J. Amer. Chem. Soc. 1897, 19, 820).

Lead fluoride PbF_2 is formed in the same way as the corresponding iodide. It is a white powder, almost insoluble in water and in hydrofluoric acid, but readily soluble in hydrochloric and in nitric acid. It yields a basic fluoride and a chlorofluoride (Fonzes-Diacon, *l.c*).

Lead tetrafluoride PbF_4 is said to be formed in a colloidal state by the action of strong sulphuric acid on the *acid plumbifluoride* $3KF,HF,PbF_4$, but has never been obtained pure (Brauner, Chem. Soc. Trans. 1894, 393). The above acid plumbifluoride is obtained by the action of hydrofluoric acid and potassium fluoride on lead tetracetate.

Paneth and Norring (Ber. 1920, 53, 1693) have indicated the existence of a gaseous *lead hydride*, obtained by the action of dilute hydrochloric acid on an alloy of bismuth and radio-lead (thorium B). The lead hydride could not be obtained by the action of acids on ordinary lead-magnesium alloys, but traces were formed by a combined electrolysis-spark process.

Lead and nitrogen. *Lead nitrate* $Pb(NO_3)_2$ is formed by dissolving litharge in nitric acid of sp.gr. 1·35. The solution is evaporated until it has the sp.gr. 1·6, and is then allowed to cool. It forms milk-white crystals from water, clear crystals from nitric acid, of sp.gr. 4·5 and dissolves in water with a reduction of temperature. It has an astringent metallic taste, detonates with brilliant sparks when thrown upon red-hot charcoal and deflagrates when triturated with sulphur. When heated it commences to decompose at 283°, and in a sealed tube at 357°, it dissociates thus:

$$Pb(NO_3)_2 \rightleftarrows PbO+O+2NO_2$$

(Baekeland, J. Amer. Chem. Soc. 1904, 26, 391; Morgan, J. Phys. Chem. 1904, 8, 416; Colson, Compt. rend. 1909, 148, 837). Lead nitrate is used in dyeing and calico printing, for the preparation of mordants and of chrome yellow. Several basic lead nitrates are known (Senderens, Bull Soc. chim. [iii.] 11, 365; Mailhe, Compt. rend. 1902, 134, 233; Peters, Zeitsch. anorg. Chem. 1896, 11, 116).

Basic lead nitrate $Pb(OH)NO_3$ is prepared by heating litharge with solution of lead nitrate. It is fairly soluble in hot water, crystallising from the solution on cooling. It is said to be a very useful decolorising agent for sugar solutions (Herles, Zeitsch. Zuckerind, Böhmen, 1896, 21, 189; Neuman, *ibid.* 183; Zeitsch. angew. Chem. 1897, 123; Pellet, Bull. Assoc. Chim. Sucr. Dist. 1897, 14, 794; *ibid* 1905, 23, 638; Horne, *ibid.* 635).

Lead nitrite $Pb(NO_2)_2$ is obtained by decomposing silver nitrite with lead chloride and concentrating the solution in a vacuum (Lang, J. 1862, 100; *see* also Chilesotti, Atti. R. Accad. Lincei, 1908, [v.] 17, i, 824). It forms yellow prisms, soluble in water, the solution on evaporation losing nitric oxide and yielding a basic nitrite A number of these basic salts are known (Chilesotti, *ibid.* 1908, v. 17, ii. 173, 288, 377, 474; Meldrum, Chem. Soc. Proc. 1908, 97).

Lead hyponitrite $Pb(NO)_2$ is a yellow crystalline powder, which explodes on heating (Kirschener, Zeitsch. anorg. Chem. 16, 424; Divers, Chem. Soc. Trans. 1899, 121).

Lead nitrohydroxylamine PbN_2O_3 is an unstable salt (Angelico and Fanara, Gazz. chim. ital. 31, [ii.] 15).

Lead imide PbNH is obtained by the action of potassamide on lead iodide in liquid ammonia. It is a reddish-brown explosive substance. If the lead iodide be in excess, a white basic salt $NPb_2I{\cdot}NH_3$ is formed (Franklin, J. Amer. Chem. Soc 1905, 27, 820).

Lead azide PbN_6 is said to be formed by the action of aqueous ammonia or of nitrides on lead salts (Curtius and Rissom, J. pr. Chem. [ii.] 58, 261).

Lead cobaltinitrite, lead cyanide, and cyanate, the corresponding thio- compounds, and lead ferro- and ferri- cyanides are known.

Lead Phosphates. *Tribasic lead phosphate* $Pb_3(PO_4)_2$ is an amorphous white powder obtained by precipitating an excess of lead acetate with a small quantity of sodium phosphate at 100° or by boiling the dibasic salt in water for 5–6 hours.

Dibasic lead phosphate $PbHPO_4$ is prepared by precipitating a somewhat dilute solution of lead nitrate with hot dilute phosphoric acid at 100°. It forms a fine crystalline powder.

Monobasic lead phosphate $Pb(H_2PO_4)_2$ is formed by dissolving the dibasic salt in strong phosphoric acid by the aid of heat and allowing the solution to crystallise. It may then be recrystallised from phosphoric acid. It forms fine needles stable in air, and is decomposed by cold and even more readily by boiling water, forming first the dibasic and finally the tribasic salt (Alders and Stähler, Ber. 1909, 42, 2261).

Lead pyrophosphates, a number of complex phosphates and *thiophosphates* (Gerhardt, Ann. Chim. Phys. 1848, [iii.] 22, 505; Ouvrard, Compt. rend. 1890, 110, 1334; Friedel, *ibid.* 1894, 119, 260; Ferrand, *ibid.* 1896, 122, 886), and also *lead phosphites* (Amat, *ibid.* 1890, 110, 901), have been prepared.

The following are naturally occurring lead phosphates and arsenates isomorphous with apatite, a portion of their chlorine often being replaced by fluorine:—

Pyromorphite $Pb_3(PO_4)_2Pb_2ClPO_4$; *Polysphærite* $(Pb,Ca)_3(PO_4)_2(Pb,Ca)_2ClPO_4$; *Mimetite* $Pb_3(AsO_4)_2Pb_2Cl(AsO_4)$; and *Kampylite* $Pb_3[(As,P)O_4]_2Pb_2Cl[(As,P)O_4]$.

Lead arsenate may be formed by suspending litharge in a solution of arsenic acid in the presence of nitric or acetic acid as catalyst (U.S. Pats. 892603, 903389, 1908; J. Soc. Chem. Ind. 1908, 1019, 1203), or by roasting a mixture of white arsenic and a lead salt in combining proportions in the presence of oxygen or an oxidising agent (U.S. Pat. 929962, 1909).

Lead arsenate is used as an insecticide and is largely employed in the United States for the protection of fruit trees from the larvæ of the gypsy moth. For this purpose, it is said to be best prepared by adding a solution of lead acetate or nitrate to sodium arsenate until an iodine test paper shows the presence of excess of lead (Haywood and McDonnell, J. Soc. Chem. Ind. 1910, 1027; *see* also Pickering, Chem. Soc. Trans. 1907, 312). The precipitate is a mixture of basic arsenate $Pb_5OH(AsO_4)_3$ and dibasic lead arsenate, $PbHAsO_4$. For other lead salts of arsenic acid, *see* McDonnell and Smith (J. Amer. Chem. Soc. 1916, 38, 2027). For spraying plants, it is often mixed with lime-sulphur solution; in this case, the normal lead salt should be employed, and it is best to avoid using water containing much alkali carbonate, as the tendency of the latter is to make the arsenic soluble (Brady and Tartar, J. Ind. Eng. Chem. 1910, 2, 328; *see* also Griffen, *ibid.* 1909, 1, 659; Moreau and Vinet, Compt. rend. 1910, 150, 787)

Lead silicates. Silica fuses with lead oxide forming a yellow glass. Lead silicate also forms a constituent of flint glass. Two silicates have been isolated (Cooper, Shaw, and Loomis, Amer. Chem. J. 1909, 42, 461). *Lead orthosilicate* Pb_2SiO_4 forms colourless hexagonal tablets, and has m.p. 746°.

Lead metasilicate $PbSiO_3$ has m.p. 766°, and has been found to exist naturally in Mexico as *alamosite*. It is analogous to *wollastonite*, calcium silicate, and occurs in radial aggregates of colourless transparent fibres (Palache and Merwin, Amer. J. Sci. 1909, 27. 399; *see* also Hilpert and Weiller, Ber. 1909, 42, 2969; Hilpert, Metallurgie, 1908, 5, 535).

Lead silicofluoride is formed by heating galena or other lead-containing material with hydrofluosilicic acid, air being blown through the mixture and water being then added (U.S. Pats. 754667, 1904; 779091, 779092, 1905). (For the use of lead silicate in glazes *v.* FRITTS and GLAZES.)

Lead borates and lead boric glasses have been prepared (Faraday, Phil. Trans. 1830, 1).

The precipitate formed by adding excess of a solution of borax to a solution of a lead salt is lead metaborate $Pb(BO_2)_2,H_2O.PbO,3B_2O_3$ is formed by fusing boric acid and lead carbonate.

Lead and sulphur. *Lead sulphide* PbS occurs in nature as *galena*, usually in the form of cubes, possessing a bluish-grey colour, and sp.gr. 7·25–7·7 (Hannay, J. Soc. Chem. Ind. 1894, 639). It may be formed by passing sulphur vapour over lead, by fusing lead oxide with excess of sulphur, or, in an amorphous condition, by passing sulphuretted hydrogen into a solution of lead nitrate. When heated in a current of certain gases, it sublimes in cubes, whilst if fused with potash and sulphur, it forms octahedral crystals.

Lead sulphide has m.p. 1120°±10° (Friedrich, Metallurgie, 1907, 4, 479; *ibid.* 1908, 5, 23); according to Lodin (Compt. rend. 1895, 120, 1164), the m.p. is 935°. It is converted by nitric acid into nitrate and sulphate, and is decomposed by hot strong hydrochloric acid, sulphuretted hydrogen being evolved. Lead sulphide forms double compounds with the halides of lead (Hunenfeld, J. pr. Chem. 1836, 7, 27; Parmentier, Compt. rend. 1892, 114, 299; Lenher, J. Amer. Chem. Soc. 1895, 17, 511; *ibid.* 1901, 23, 680), and also with bismuth sulphide (Ducatte, Compt. rend. 1902, 134, 1061). The reactions between lead sulphide and its oxidation products have been studied in detail by Schenck and Rassbach (Ber. 1907, 40, 2185, 2947; *ibid.* 1908, 41, 2917).

A *polysulphide* PbS_5 is formed as an unstable purple-red precipitate by precipitating lead nitrate at 0° with calcium pentasulphide and washing the precipitate with carbon disulphide (Bodroux, Compt. rend. 1900, 130, 1397).

Lead sulphate is found native as *lead vitriol* or *anglesite*, in transparent rhombic crystals isomorphous with *celestine* and *heavy spar*. It may be obtained as a white powder by precipitating a lead salt with sulphuric acid or with a soluble sulphate, or by the action of sulphur dioxide on lead peroxide (Marino, Zeitsch. anorg. Chem. 1907, 56, 233). It may also be obtained crystalline (Manross, Annalen, 1852, 82, 360). Lead sulphate has sp.gr. 6·2–6·3, and is said to melt without decomposition at a red heat, but according to Schenck and Rassbach (*l.c.*) it does not melt below 1100°. It is soluble in pure water to the extent of 0·0824 gram of lead sulphate per litre or 1 in 12135 at all temperatures, but the solubility diminishes on addition of sulphuric acid (Sehnal, Compt. rend 1909, 148, 1394; *see* also Dolezalek and Finckh, Zeitsch. anorg. Chem. 1906, 51, 320). Lead sulphate is also soluble in alkalis, in ammonium and in calcium acetates, and in a number of other salts (Long, Amer. Chem. J. 22, 217; Reichard, Chem. Zeit. 1903, 27, 924, 943; Fox, Chem. Soc. Trans. 1909, 878). It forms double salts with the sulphates of tin (Weinland and Kühl, Ber. 1906, 39, 2951); with potassium (Belton, Chem. News, 1905, 191); and with arsenic (Kühl, Arch. Pharm. 1907, 245, 377). It is reduced by carbon at 550° and by carbon monoxide at 600°–650°, lead sulphide being formed; this reacts with unaltered sulphate yielding lead and sulphur dioxide.

Lead disulphate or *Plumbic sulphate* $Pb(SO_4)_2$ is obtained at the anode when pure sulphuric acid, of sp.gr. 1·7–1·8 is electrolysed between lead electrodes. It is a white or faintly greenish-yellow crystalline powder, giving a green solution in strong sulphuric acid. It is decomposed by water, forming sulphuric acid and lead peroxide, and is a powerful oxidising agent. It forms double salts with the alkali metals and also with aniline and with dimethyl and diethyl aniline (Elbs and Fischer, Zeitsch. Elektrochem. 1900, 7, 343). On the preparation and use of basic lead sulphate, *v.* above.

Lead sub-sulphate is a dark grey substance decomposed by water, prepared by heating lead sub-oxide in methyl sulphate vapour at 280° (Denham, Chem. Soc. Trans. 1919, 109).

Lead sulphite and *lead thionates* are also known.

Lead selenide (Pélabon, Compt. rend. 1907, 144, 1159); *selenites* (Marino, Zeitsch. anorg. Chem. 1909, 62, 173); and *selenates* (Mathers, J. Amer. Chem. Soc. 1908, 30, 1374), also exist.

Lead organic compounds. The lead alkyl compounds are prepared by the interaction of alkyl iodides and lead-sodium or by the action of lead chloride on zinc alkyls (Buckton, Annalen, 1859, 109, 222; Cahours, *ibid.* 1862, 122, 65; Ghira, Gazz. chim. ital. 24, i. 44, 320; Frankland and Lawrence, Chem. Soc. Trans. 1879, 245; Klippel, J. 1860, 383).

Lead ethoxide $Pb(OEt)_2$ has been prepared by suspending thin sheets of lead over absolute alcohol through which a stream of ozone is passed. When washed with alcohol and dried *in vacuô* over sulphuric acid, it forms a light yellow friable powder, soluble in, but readily hydrolysed by, water (Perkin, Chem. Soc. Proc. 1908, 179).

Lead tetraphenyl may be obtained by the action of lead chloride on an ethereal solution of magnesium phenyl bromide (Pfeiffer and Truskier, Ber. 1904, 37, 1125; Polis, Ber. 1887, 20, 3332).

Lead tricyclohexyl $Pb(C_6H_{11})_3$ is prepared by the addition of lead chloride to a solution of magnesium cyclohexyl bromide in dry ether. It forms yellow, hexagonal plates, decomposing at 195°, and combines with iodine at the ordinary temperature to form the iodide $Pb(C_6H_{11})_3I$, from which the hydroxide and other compounds can be prepared by the usual methods. The molecular weight determined cryoscopically agrees with the formula given above, so that the triaryl may be regarded as containing tervalent lead, and thus analogous to Gomberg's triphenylmethyl (E. Krause, Ber. 1921, 54, [B], 2060). A number of other aromatic and aliphatic alkyl and halogen alkyl compounds have been prepared (Pfeiffer and Truskier, *l.c.*; Polis, *l.c.*, and 717).

Lead thiocarbamide halides $Pb(CH_4N_2S)_2X_2$ ($X = Cl, Br, I$) are described by Rosenheim and Meyer (Zeitsch. anorg. Chem. 1906, 49, 13).

For the lead salts of organic acids, *see* the respective acids. J. A. S.

LEADHILLITE. A rare mineral approximating in composition to the formula

$$PbSO_4{\cdot}2PbCO_3{\cdot}Pb(OH)_2$$

The monoclinic crystals have the form of six-sided plates or pseudo-rhombohedra with a perfect basal cleavage and pearly lustre. As indicated by variations in the optical characters and chemical composition, there appear to be at least three varieties or modifications. The mineral is found in the upper oxidised portions of veins of lead ore at but few localities, notably at Leadhills in Scotland. It has also been met with in lead slags left by the Romans. 'Susannite' is a variety from the Susanna mine at Leadhills, and the name 'maxite' has been applied to crystals from Sardinia. L. J. S.

LEAF GREEN. *Chrome Green* (*v.* PIGMENTS).

LEATHER. When the skins of animals are treated with infusions containing any of the vegetable tannins, the gelatinous tissue is converted into the tough imputrescible substance known as leather, while the process by which it is made is called 'tanning.' Certain mineral salts, as well as oils and fats which undergo oxidation in the skin, have a somewhat similar effect, and more recently, aldehydes, and especially formaldehyde, have been successfully employed. Synthetic condensation products of phenolic sulphonic acids with formaldehyde with marked tanning properties (Syntans) have been invented by Stiasny, and have come largely into practical use; and a number of other substances, aromatic derivatives, colloidal precipitates, and even elements such as bromine have proved capable of converting skin into leather. It is proposed in the following article first to describe the structure and chemical composition of skin, and the preliminary processes it has to undergo to deprive it of hair and to render it fit for tanning, and then to deal with the different tanning materials and the various processes by which they are employed in practice.

The skin, as it exists on the animal is much more than a mere covering, and contains a variety of organs, both of sense and of secretion, and some knowledge of its anatomy is necessary to a proper understanding of the tanning process.

The skin consists of two layers, which arise in embryonic development from the inner and outer layers of the ovum, and which throughout retain the strongly marked differences which correspond to this diversity of origin. The *epidermis* or outer layer of the skin is derived from the outer layer (epiblast) of the ovum, while the inner layer, *corium*, *derma*, or *cutis*, together with all the other connective tissues of the body, takes its rise from the middle of the ovum (mesoblast). Though the skins of different animals differ in details, that of the calf, of which a section is illustrated in Fig. 1, may serve as a type of most of those used in the manufacture of leather. The outer layer or *epidermis* consists, as has been said, of simple nucleated cells, which at the surface are dead, hardened, and flattened, but where they rest on the *corium* are soft and spherical, and constitute the so-called 'mucous layer' (*rete mucosum*). This is not supplied directly with blood-vessels,

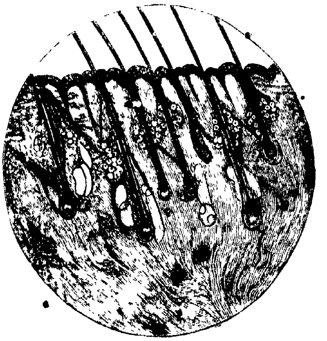

Fig. 1.

but derives its nourishment from the fluids of the *corium*. Here growth takes place, and the cells probably multiply by fission, though this has not been actually observed. The hairs, though deeply rooted in the *corium*, are really products of the *epidermis* which surrounds them and passes down into the *corium* in the form of a bulb-shaped sheath. The nourishment of the growing hair is supplied by a knob of connective tissue called the hair-papilla, furnished with blood-vessels, and passing up into the centre of the hair-bulb. The hair itself is composed of modified and hardened cells, forming exteriorly irregular overlapping scales, giving the outline a serrated appearance, which is especially marked in wool. Within this 'hair cuticle,' as it is sometimes called, is the fibrous portion of the hair, composed of long spindle-shaped cells, and sometimes in the centre of this is a cellular pith containing air. The hair, except in white animals, contains a good deal of pigment, and some is also present in the epidermis cells forming the hair-sheath The new hair, both in fœtal development and in ordinary growth, begins as a thickening of the *epidermis* layer, forming a knob which gradually sinks into the *corium*, and becomes a bulb in which the hair is developed and forces its way to the surface much as an onion does to the surface of the ground. In animals which change their coats in spring, the young hair generally originates in this way from a new bulb formed below the old one, and passes up into the old sheath. This deep-seated origin explains the great difficulty found in removing these young hairs for technical purposes. Besides the hairs, sudoriferous and sebaceous glands are similarly developed from the *epidermis*. The sebaceous glands are seated round the stems of the hairs, and their ducts discharge oily matter which serves as a lubricant into the hair sheaths near the surface of the skin. The sudoriferous glands are more deeply placed, usually extending even below the hair roots; they are less convoluted than in man, and discharge through narrow sinuous ducts to the surface.

The *corium* consists mainly of connective tissue, which, on boiling with water, readily dissolves, and is wholly converted into gelatin. In most animals the principal part of the hide (*pars reticularis*) is composed of bundles of interlacing fibres, each of these bundles being formed of a multitude of fine fibrils. Towards the outer surface these bundles disappear, and the separate fibrils combine in a closely-matted felt (*pars papillaris*), which is technically known as the 'grain.' In the pig, and possibly also in the seal, this close-textured part is thick, and is all that is valuable for tanning, the reticular part being so slightly developed as not to be distinguishable from the looser fatty tissue (*panniculus adiposus*), which underlies the true skin. Consequently, these skins are remarkable for extreme toughness. In addition to this gelatinous structure, the true skin, and especially the grain or papillary part, contains certain yellow fibres called 'elastic,' and distinguished by their very difficult solubility in boiling water, acids, and alkalis. These fibres are digested and removed by tryptic ferments, which do not attack the white connective tissue, but not by peptic ferments which attack both. The removal of the elastin is one of the principal objects of "puering," which is now frequently accomplished by pancreatic extracts combined with ammonium chloride.

Between the *corium* and the *epidermis* is an extremely fine membrane or outer surface, known as the hyaline This is very difficult to demonstrate microscopically, but has been separated in some technical operations, and is probably the cause of the clear brown or buff colour of the grain surface of tanned leather, while the finely matted tissue below it remains nearly white.

The *corium* has also blood-vessels, nerves, and minute muscles for erecting the hairs; but none of these of much technical importance, and for further details the reader may be referred to Procter's Leather Industries Laboratory Book, his Principles of Leather Manufacture, or to an important series of articles by Seymour-Jones in the Journal of the Society of Leather Trade Chemists during 1917 and 1918.

A few words must, however, be said about the practical microscopic examination of skin. For this purpose it is necessary to produce extremely thin sections, and the skin must be previously hardened. To this end it may be cut into strips about ½ inch long by ¼ inch wide, with their length at right angles to the direction of the hair, which should be cut short with scissors, with which also the loose fatty subcutaneous tissue should be removed. The strips are placed in a closed vessel with several times their volume of methylated spirit diluted with an equal quantity of water. The next day this must be replaced by stronger alcohol, and finally by absolute. In 4–8 days, the hide will be hard enough to cut, and may be held between the finger and thumb, and shaved by a drawing cut with a very sharp razor flooded with alcohol and resting on the tip of the forefinger. The cut should begin at the grain side, and must be exactly parallel with the hairs to give good results. For this reason a microtome is of very little service, as it is more difficult to adjust the fragment of hide in it than to make the sections by hand. They are floated off the razor in alcohol, and must be stained in order to make the details visible. Various methods of staining are described in the microscope text-books, one of the simplest being to immerse in aqueous solution of picrocarmine. The carmine stains the connective tissue and the nuclei of the cells red, while the structures derived from the *epidermis*, the *erectores pili* muscles, and the blood-vessels, absorb the picric acid only, and become yellow. The section may now be soaked in glycerol to clear it, and examined in a drop of glycerol under a thin cover-glass; or may be permanently mounted in glycerol or Farrant's fluid; but for this purpose it is generally better, instead of clearing with glycerol, to soak the sections again for some time in absolute alcohol containing a little picric acid, till quite deprived of water, clear in clove oil, and mount in a drop of solution of gum dammar in benzene, or of Canada balsam.

Kathreiner has described a method which, while it is less striking for demonstration of the different tissues, is often useful for practical work when a knowledge of the general appearance of the structures has been attained. The fresh hide (and it is important in preparing type specimens that the animal should not have been killed more than a few hours) is cut into small strips as described, and then immersed for 4–8 days, according to the thickness of the hide, in about twelve times its volume of an aqueous solution containing 1 p.c. of osmic and 2½ p.c. of chromic acids. This solution must be kept from light and dust in a stoppered bottle and in a cool place. Care must be taken to avoid the fumes, which cause severe catarrh of the mucous *membranes*. The hide pieces must now be soaked in about twelve times their volume of absolute alcohol several times renewed for 4–8 days, and are then cut as described. No further staining is required, as the chromic acid colours the tissues yellow, while all traces of fat, as for instance, the oily matter of the sebaceous glands, are stained grey or black by the osmic acid. They may be cleared at once with clove oil, in which they may be examined, or mounted in dammar.

A third method may be mentioned which is very useful for rapid observations, especially when it is desired to ascertain how far the cellular structures have been affected in preparing the hide or skin for tanning. The section, which need not be so thin as when intended for more detailed study, may be cut either after a short hardening in alcohol, or in the case of hide swollen with lime, simply by cutting a small strip ¾ through from the grain, and turning it back so as to put the tissue on the stretch, and then cutting from flesh to grain with a razor flooded with distilled water. If the wet section be placed in a drop of water on a slide under a cover glass, and examined by reflected light with a 1-inch objective, the fat glands will be seen as yellow masses embedded in the white fibrous tissue. If now the section be moistened with a mixture of equal parts of glycerol and glacial acetic acid, the connective tissue will become quite transparent, and the glands and hair-roots may be examined, even with a moderately high power, by transmitted light. For more minute study several improvements in technique, and especially in staining methods, have recently been made, with regard to which original papers, mostly in the Journ. of Soc. of Leather Trades Chemists, must be consulted.

The principal chemical constituents of the skin are proteids, fats, and water, and the most important of these is collagen, of which the white fibres, forming the main fabric of the hide, are composed, and which, on boiling with water, is converted into gelatin (glutin). The remaining proteids (keratins, elastins) are mostly albuminoids, but glycoproteins (mucins) and those of the blood and lymph (serum albumens, hæmoglobin, &c.) are also present.

The *epidermis* and its products, hair, horns, hoofs, &c., all belong to the class of keratins, which are allied to coagulated albumen, but differ in their composition (*e.g.* in their percentage of sulphur), and in their behaviour towards chemical reagents. They can hardly be said to be soluble in water, though by prolonged boiling under pressure they are finally dissolved to an extract which does not gelatinize on cooling. The softer structures are easily soluble in dilute caustic alkalis in the cold, whilst hair and horn are gradually softened, but only yield to strong solutions aided by heat. They are reprecipitated by acids, and these precipitates mixed with oil have been proposed as a 'filling' for alumed leather in place of flour and egg-yolk, but have not come into practical use. Lime and other alkaline earths act like the alkalis, and hence milk of lime, while it scarcely attacks the hair, easily loosens it, by dissolving and softening the *epidermis* and root sheaths. Strong solutions of the alkali and alkaline-earth hydrosulphides, on the other hand, seem to attack the harder tissues by preference, and reduce the hair to pulp without affecting the *epidermis* cells so much as milk of lime.

Collagen forms nearly 95 p.c. of the dry matter of the *corium* and is insoluble in cold water, dilute acids, and common salt solution (Reimer's statement that it is soluble in 10 p.c. solution of NaCl has not been confirmed), and it is but slowly attacked by dilute alkaline solutions, but strong acids and alkalis have a hydrolysing action, yielding soluble products. Boiling water has a similar effect, the first stage in this case being gelatin, which is slowly further attacked, continued hydrolysis yielding hemicollin and semiglutin, and later gelatoses and glutin peptones.

Hofmeister, who has studied these changes, proved that the production of gelatin from collagen is merely hydrolytic, with an increase of weight of about ¾ p.c. As final products of prolonged hydrolysis, ammonia, and amino-acids are formed, among the latter, glycine (amino-acetic acid), glutaminic acid, leucine (amino-caproic acid) arginine, lysine and *α*-proline being the most important, while tyrosin and tryptophan are absent. Thus all the products of collagen belong to the antigroups of proteids, and aromatic groups are almost absent, in this respect showing a marked difference from keratin and the albumins.

Hydrolysis of collagen is also produced by pepsin (in slightly acid solutions), but trypsin has no dissolving action on collagen unless the latter has previously been treated with water at 70° or with acids. Putrefactive bacteria rapidly lead to the final products of hydrolysis (amino acids, &c.)

Elastins form the substance of the 'yellow' or 'elastic' fibres which act as a sort of soft framework to the connective tissue, and are remarkable for their great resistance both to putrefaction and to chemical reagents. They are digested by active tryptic ferments.

Mucins are present both in the mucous layer and in the substance which cements the fibrils into fibre-bundles. The nature of this interfibrillar substance, called corim by Reimer, has been much disputed. Rollet,[1] who first studied it, considered it of a mucous nature, but Reimer[2] claimed that it differed from mucins, and was a hydrolysis-product of the fibres themselves. Körner[3] held a similar view, taking it to be collagen rendered more soluble in alkalis by swelling and hydration. Both Halliburton[4] and Van Lier,[5] on the contrary, favour its mucin character, and the latter names it coriomucoid (in distinction from tendo-mucoid). The mucins are easily soluble in even dilute alkaline solutions, and are dissolved during the process of liming, allowing the epidermis to be mechanically removed and isolating the fibrils.

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[1] Sitz Ber. Wien 1858, 30, 37.

[2] Dingl polv J. 205, 143.

[3] Jahresbericht der deutscher Gerberschule, Freiberg, 1898.

[4] Jour. Pathol. & Bacteriol. 1892, 1.

[5] Zeitsch. physiol. Chem. 61, 1909.

Fats.—A distinction must be made between those of the *epidermis*, which are largely unsaponifiable, and consist mainly of cholesterols and liquid waxes; and those of the fat-cells of the *corium*, which are almost entirely triglycerides like most ordinary fats. The former exist not only as products of the sebaceous glands (wool-fat, &c.), but are combined with the keratins, rendering the *epidermis* more resistant, and thus fulfilling a similar function to the waxes in plants (Liebreich[1]). The fats of the *corium*, like those of the body, vary in composition, and especially in the proportion of olein to stearin and palmitin, with the age, sex, and food of the animal, but are usually of lower melting-point than the corresponding internal fats. They are liquid during life, but in warm-blooded animals solidify after death.

Fresh hides and skins contain 50–70 p.c. of water, of which the larger proportion is in the *corium*, and the total is highest in young animals. In the adipose tissue below the skin, the proportions of fat and water are approximately equal.

Hides and skins reach the tanner in various states. Most of those from animals killed in this country are either fresh or very slightly salted, but those from greater distances are treated in various ways to preserve them. Perhaps the simplest and best is the use of salt, either sprinkled on the flesh side repeatedly, or used in the form of brine. In this way most European hides, and many of those from North and South America, are cured. In countries remote from the sea, hides are frequently first salted and then dried, so as to save weight in carriage, and at the same time to preserve them better. This is called 'drysalting.' A still commoner method, especially where salt is scarce and costly, is simply to dry the hide or skin either by hanging in the shade or by stretching on the ground in the sun. Many hides from Texas and Central and South America are thus treated, as well as smaller skins from more temperate countries. The hides of the small cattle of India, called 'kips,' are plastered on the flesh side with a mixture of a native saline earth containing sodium sulphate and water, to preserve and, incidentally, to weight them, and then dried. Sometimes an addition of arsenic is used to prevent the ravages of insects. It has been proposed in Germany to substitute sodium sulphate for common salt in the curing of skins, both on account of the tax on salt, and because the former retains water, and consequently increases the weight of the hide. The advantage of this to the tanner does not seem obvious. In Russia and other cold climates, hides are sometimes preserved by freezing.

Preparation of hides for tanning.—Preliminary to any other treatment, it is necessary to soften hides and skins, and to free them from blood and dirt. When fresh, a few hours, or at most a day or so in one or two changes of fresh water is sufficient to accomplish this; and for sole leather the cleansing does not need to be so thorough as for the finer sorts, whilst too long soaking is apt to lead to incipient decomposition, and to yield a soft and light-weighing product. Where goods are salted, a much more thorough washing is desirable, and it is advisable to give three or four changes of water to remove the salt as rapidly as possible, and to swell the tissue, which is more or less dehydrated by salting. A final treatment in a washing drum with running cold water is often useful.

When hides have been dried, a mere soaking is in most cases insufficient to produce complete softening, and in addition mechanical and chemical means have to be employed. Eitner has pointed out that the higher the temperature at which the original desiccation took place the greater is the difficulty of softening; calfskin which has been dried at 60° refusing to soften sufficiently for tanning either by soaking or mechanical means. This is analogous to the fact that gelatin dried at 130° becomes insoluble even in boiling water. For thin skins, such as calf or sheep, dried in the open air in temperate climates, a simple soaking of some days in cold fresh water, assisted by working over the beam with a blunt knife, is enough. On the other hand, for the sun-dried kips of India or the heavy ox hides of Texas and South and Central America, such treatment would be quite ineffectual, and the method was formerly adopted in this country of soaking for 2 or 3 weeks in water, which being seldom changed and highly charged with organic matter from previous parcels of hides, was in a state of active putrefaction. Such soaks will soften much more rapidly than fresh water, and are effectual where even prolonged treatment with it would fail. In India, hides are softened by the native tanners within 24 hours, by plunging them into pools in which all the refuse of the tannery is allowed to collect and putrefy. It has, however, come to be recognised by observant tanners that this putrid soaking is very dangerous and unsatisfactory, especially where the hides are destined for sole leather, since it has always a destructive effect on the tissue, and it is found that a much more rapid and satisfactory softening may be effected by the use of very dilute solutions of sodium hydroxide, or sodium sulphide, or of weak acids. A solution of sulphurous acid of about N/20 strength followed by cold water, has been successfully used, and from its antiseptic effect, seems particularly suited for hot climates. When the hides or kips were so far softened that they could be bent sharply without danger of breaking the fibre, they were worked in the 'stocks' or 'hide-mill,' which is a machine in which two large hammers or plungers work the hides with a sort of kneading action, but this violent treatment has been rendered unnecessary by the chemical treatment, and at most a drumming with warm or tepid water in a rotating 'tumbler' like an immense barrel-churn is all that is needed. A machine in use on the Continent for the same purpose consists of two rollers studded with rounded pegs, or of which one is grooved and the other pegged. The hides are passed back and forwards between these, and undergo a sort of kneading action. When the hides or skins are thoroughly softened they are ready for depilation.

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[1] Virchow's Archiv. 121, 183.

Depilation.—With a few exceptions, which scarcely come properly under the head of 'leather,' it is necessary to remove the hair preparatory to the tanning process. Probably the oldest way of doing this is by putrefaction, or as it is technically called, 'sweating.' This was formerly accomplished by leaving the hides or skins, folded or laid together, in a warm and moist place, till the destruction of the *epidermis* liberated the hair. But though the *corium* was somewhat more resistant to putrefaction than the mucous layer of the *epidermis*, the putrefactive change frequently spread into it, and injured at least its surface. This simple form of sweating may now be considered obsolete, and where putrefaction is still employed, it is by what is known as 'cold sweating,' which, though little used in England, is still employed in America in the treatment of dried hides. In this method the hides are suspended from tenter-hooks in well-ventilated chambers, usually almost buried in soil or spent tan, so as to maintain an equable temperature (which is generally somewhere between 15° and 20°, the higher the more rapid being the action). The air is kept saturated with moisture, and the temperature regulated by admitting steam under a false bottom, or a spray of water from pipes provided for the purpose. The hides, which if dried must previously have been thoroughly softened, are ready for unhairing in 3-7 days, and during the latter part of the time must be examined from hour to hour, and, as soon as the hair is loosened, taken down and placed in piles on the floor. As the thick parts take longer to unhair than the thinner, and the process proceeds more rapidly at the top than the bottom of the chamber, the position of the hides must be altered as the action progresses. When the hair is fully loosened, it is removed either by scraping with a blunt two-handled knife on a sloping 'beam,' or by fulling with stocks. Some American tanners now give a light liming before unhairing to slightly plump the goods and check the decomposition. The sweating or 'staling' process is largely employed in Europe for unwoolling sheepskins; in this case to avoid the injurious effect of lime upon the wool. The process is not wholly bacteriological, since ammonia, which is largely evolved, acts as a caustic alkali on the epidermis and is itself capable of loosening the hair without putrefaction.

In England, both for sole and dressing goods, the hair is almost universally loosened by the use of lime. The pits are usually, though by no means invariably, worked in sets of three, of which one is old and nearly exhausted, the second fairly good, and the third freshly made or strengthened. The duration of the process is very variable, ranging from 4 or 5 to 14 days or more, and the quantity of lime used is yet more indefinite, being variously stated at from 1 lb. to 12 lbs. per hide. The fact is, that, lime being very scantily soluble in water, any quantity beyond that required to maintain a saturated solution has but little effect. Lime is only soluble to the extent of about 1¼ oz. per cubic foot, but of course is continuously absorbed by the hide, so that an excess is required which may be less the more often the hides are moved and brought in contact with fresh portions of the lime liquor. Hides lime well and rapidly, suspended from frames in pits, especially if rocked or frequently shaken, and in any case the more frequently they are moved, the better and more uniform is the action; mechanical motion is largely in use on the Continent, and to an increasing extent in England, the solution being generally kept in motion round the suspended hides by the use of compressed air, by which the time required is much shortened and the solution of hide-substance is lessened. In America, the hides are usually tied together by the shanks and wound from one pit to another over a 'reel' or skeleton drum, turned by hand or power. The old lime liquors become charged with ammonia and organic products from the hides, which materially modify their action, rendering more lime soluble, but diminishing its plumping effect. One result of this is that hides unhair more readily out of a somewhat old lime than they do out of one freshly made, and a change from an old into a newer and stronger lime sometimes actually sets the hair firmer at first, by plumping the tissue and so grasping the root-bulbs. Experiments seem indeed to render it probable that lime alone in the complete absence of putrefaction, will not loosen the hair in any reasonable time. If hides be limed for 1 to 4 days in a sharp new lime in which they are frequently drawn, and are then transferred into a pit of water maintained at a temperature of 40°-50° for some hours, they will part readily with their hair, and at the same time be to a considerable extent freed from lime. This plan, which is of American origin, and is sometimes called the 'Buffalo method,' may be highly recommended for sole leather, giving good weight and colour and a firm solid texture. Of course, the relative amount of liming and hot water may be varied to a considerable extent.

Unhairing may also be hastened by warming the limes themselves. The heat increases the solubility of the hide, but at the same time checks the plumping, and the tendency is to produce a soft and porous leather. Hence the method is ill adapted for sole, and even for dressing leather is undesirable, since the same effects are obtained better in other ways.

It has naturally been proposed to substitute the caustic alkalis for lime, and it is probable that it might be done in some cases with advantage, or at any rate that small quantities might be added to the limes to hasten their action; but so far their use has not found much favour with tanners, except as constituents of such secret preparations as 'Inoffensive.' One cause of this is probably that from their easy solubility and powerful action, great care is required, and where used by 'rule of thumb,' serious injury is readily done to large quantities of costly raw material. It is one of the virtues of lime that, from its very limited solubility, it is almost impossible to destroy a pack of hides by its use, and the injury which it does when carelessly handled is often attributed to other causes. It has recently been shown by J. Loeb that, in accordance with the Procter-Wilson theory of swelling, the swelling power of divalent alkalis, such as lime and baryta, is for the same hydroxyl ion concentration, only about half that of the monovalent such as soda and potash.

Naturally it might be thought that the alkalis would be easily removed from the hide by simple washing, and that the solubility of their soaps would favour the removal of grease; but it is found that alkalis form a sort of compound with hide-fibre, from which they can scarcely be removed until they have first been neutralised with acid, while practically the grease is not saponified but merely emulsified, and for this purpose lime answers just as well as a stronger alkali.

In liming sole leather the principal object is to enable the hair to be removed and to free the hide from grease with as little solution of its fibrous structure as possible. The English tanner frequently desires also to raise or swell the hide, and so to split up the fibrous bundles into their constituent fibrils as to prepare it for tanning, though this may also be done by the presence of acid in the earlier tanning liquors, or in some cases by the direct use of an acid bath. It is a question on which there has been much difference of opinion whether the unhairing is best accomplished by the use of strong fresh limes for a short time, or of old limes charged with ammonia for a longer period. It is now, however, generally recognised that the continued action of old limes is too dangerous, usually injuring the grain surface of the hide or skin, and the compromise is usually adopted of beginning the process in the older limes and finishing in fresh ones. It is very dangerous in hot weather to let limes get too stale and loaded with organic matter, as in this case even the presence of caustic lime does not prevent putrefaction, which is fatal to the manufacture of plump and solid leather. In fact, by microscopic examination of such stale limes it is easy to detect the presence of active bacteria. It is a mistake to suppose that such limes are 'weak,' since the excess of lime is always sufficient to maintain them as saturated solutions, and in addition they contain much dissolved lime as organic salts, and considerable quantities of ammonia and bacterial enzymes, which, though they lessen swelling, assist in the solution of the hide. If in any case the liming is too low, it will be impossible to eradicate grease from the hides of very fat cattle, although the leather may be of excellent quality. In the manufacture of dressing leather a somewhat more thorough liming is generally desirable, since it is not only required to remove the hair but to dissolve a proportion of the cementing matter of the fibrous tissue, and so render the leather softer and more pliable. This is especially true in the manufacture of glove or 'glacé' kid and lamb leather, in which the property of stretching in any direction is largely dependent on a proper liming. In the continental manufacture of these goods it is customary to 'sharpen' the limes by the addition of realgar (arsenic sulphide). This produces, with the lime, dicalcium hydrosulphide, sulpharsenate, and some metallic arsenic, and considerably hastens the unhairing. Orpiment, the yellow arsenic trisulphide, may also be used. The calcium sulphydrate is the active agent, V. Schroeder and Schmitz-Dumont (Dingl. poly. J. 1896) having shown that the arsenic compounds are inoperative and not even antiseptic; and, many years since, the desirability of finding a substitute for the very poisonous red arsenic led Böttger to propose the use of calcium hydrosulphide, prepared directly by passing sulphuretted hydrogen into milk of lime. This produces a paste which is greenish from the presence of traces of iron sulphide, and which acts as a rapid depilatory, and if applied as a paste on the hair-side will in a few hours reduce the hair to a pulp, whilst from the rapidity of the action, the hair bulbs and the various glands are much less affected than with an ordinary liming. Mixed with lime in smaller proportion and used in pits in the ordinary way, it loosens the hair rapidly without actually destroying it, principally by attacking the mucous layer, since the harder part of the epidermis frequently comes off with the hair roots in it in sheets of considerable size. Unfortunately for its use in practice, for which otherwise it is excellently fitted, it keeps very badly, and must be freshly made as required which is both costly and troublesome. A concentrated solution of calcium hydrosulphide was formerly produced by the Washington Chemical Company, and promised to be a valuable depilatory; but unfortunately its manufacture proved unremunerative. Gas-lime, which often contains a considerable quantity of calcium hydrosulphide, has been used as a substitute, but is too uncertain in its composition to be satisfactory, and has been almost superseded as a gas-purifying agent by oxide of iron. None of these disadvantages attends the use of sodium sulphide, which has been strongly advocated by Eitner, late Director of the Austrian Government Research Institute at Vienna, to whom the leather trade probably owes much of its impulse to scientific improvement. It is now manufactured commercially, in a crystallised form; it keeps well and possesses great depilatory powers, both alone and in union with lime, with which it forms calcium hydrosulphide and caustic soda. A paste containing 2-4 lbs. to the gallon of water, and thickened with lime to a soupy consistence, will, if painted on the hair side of a hide, completely destroy the hair in a few hours, so that it may be swept off with a stiff brush. This mode of proceeding has been much recommended for sole leather, and it makes a firm and solid article, but the difficulty of getting it so thoroughly brushed into the hair that it will destroy every part of it, is very considerable, while, if any part has been missed, the short hair is very difficult to remove. For this reason, and because it leaves all the hair-roots and glands in the skin and so prevents a clean buff, it is only suitable for very common classes of leather, though it will do good service on dried hides instead of the cold sweat. Such a paste is also much used for unwooling sheepskins, being in this case applied to the flesh side and allowed to penetrate the skin. Used in pits with lime to the extent of ¼–½ lb. per hide, sodium sulphide does not materially injure the hair, while it quickens the unhairing and yields good weight and excellent quality. Strong solution of sodium sulphide or even of caustic soda does not swell from its dehydrating effect, but hides so treated swell rapidly if subsequently placed in water. Where plumpness is not desirable, but a tough, solid texture is required, as in some descriptions of light leathers, its use would promise special advantages. Since sodium sulphide, however, dissociates in solution to sodium hydrosulphide and sodium hydroxide, the effect of the latter leads to more swelling of the grain than is desired, and it is found that this may be lessened by the addition of an equivalent quantity of calcium chloride which substitutes calcium hydroxide for sodium hydroxide with formation of common salt, and enables the production of leathers with much finer grain than with sodium sulphide alone.

The total soda existing in commercial sodium sulphide as sulphide, carbonate or hydroxide may be determined with standard acid, using methyl-orange as an indicator, since this colour is quite unaffected by the presence of either hydrogen sulphide or carbon dioxide. The sulphur is advantageously estimated by ammoniacal zinc solution, using alkaline lead tartrate as an indicator by placing drops of it and of the solution being tested near each other on filter paper. Solutions containing sodium sulphide together with dissolved sulphur and polysulphides obtained by boiling sulphur with caustic soda or soda ash and lime possess considerable depilatory power, but it is not easy to determine the amount of available sulphur. Somewhat similar solutions are obtained by forcing air through the 'tank waste' of the Leblanc alkali process, suspended in water, or, naturally, in the 'bog-liquor,' which in some works drains from the waste-heaps, and where this can be cheaply obtained, it may in some cases be used advantageously.

Examination of lime liquors.—Considerable information may often be obtained by a simple examination of lime liquors. Free ammonia may be determined by rapid distillation of, say, 30 c.c. of the filtered liquor, preferably with the addition of a little magnesium sulphate to remove caustic lime. The ammonia is absorbed in a measured quantity of standard acid which is titrated back with caustic alkali. If it be desired to estimate free lime in the same sample, the magnesium sulphate must be omitted, which, if the distillation is short, does not lead to serious error. The sample should be drawn from the middle of a lime pit well plunged up, and rapidly filtered in a funnel covered with a clock-glass.

The caustic lime in the portion from which the ammonia has been withdrawn may now be estimated with normal or decinormal acid, using phenolphthalein, and the total lime (and any other alkalis present) existing in a free state or in combination with organic matter and weak organic acids with methyl orange or red as an indicator. Litmus is unsuitable for the purpose from the presence of these weak organic acids, which render its end-reaction quite indefinite, but do not affect methyl-orange so much. For the same reason this indicator will be found very useful for many determinations required in a tannery. Phenolphthalein cannot be accurately used in presence of ammonia. An estimate of the organic matter present is obtained by evaporating 50 c.c. of the filtered liquor to dryness in the water-oven in a platinum crucible, weighing, and then igniting and estimating by loss. This method can of course lay no claims to strict accuracy, but is sufficient to give valuable information as to the condition of the liquor; and, if a uniform course of liming be adopted, as to the amount of matter dissolved out of the hides in the process, or the comparative quantities by different liming methods. For more accurate work the liquor may be evaporated to dryness or very small bulk in a flask with the addition of a little excess of sulphuric acid to retain ammonia, and the nitrogen estimated by Kjeldahl's method. It is easy to calculate very approximately the amount of matter which the nitrogen represents, since both the gelatinous and horny tissues contain about 17·5–18 p.c. of nitrogen. During recent years much attention has been devoted to the more complete analysis of lime-liquors, but the literature is too extensive to be summarised here, and the reader is referred to the pages of 'Collegium,' the 'American Leather Chemists' Journal,' and especially to recent issues of the 'Journal of the Society of Leather Trades Chemists.'

Bating and drenching.—If lime or other alkalis have been used in depilation, they must be removed before tanning, and in sole leather it is desired to do this with as little loss of pelt as possible. Formerly a mere suspension in water was considered sufficient, and when the water is hard, a little lime was added to remove the free carbonic acid and calcium hydrogen carbonate present, which would form insoluble carbonate with the lime contained in the hide, and afterwards by combining with tannin would produce discoloured leather. A further cleansing may be effected by 'scudding,' or working the grain-side with a blunt knife on a beam, which expresses much of the *débris* of hair-roots and fat glands, as well as lime. When a clean buff is desired this precaution should never be omitted.

It is, however, impossible really to remove the whole of the lime by soaking in water, since it forms a loose compound with the fibrous tissue, from which it can only be dislodged by the aid of acids, and at present, even for sole leather, acids are usually employed after removal of as much lime as possible by washing in 'softened' water.

Very dilute sulphuric or hydrochloric acid will perform the service satisfactorily, although great care has to be used to keep the hides in constant motion, to add the acid in small successive doses as it is absorbed by the hides, and to avoid even a small excess. Some trouble is often experienced in the use of commercial acids from the precipitation of the iron which they contain as an impurity on the fibre of the hide, where it subsequently produces stains by combining with the tannin. The ammoniacal salts of the stronger acids may also be used, but boric, formic, acetic, lactic, and other organic acids are generally employed in solutions not exceeding about N/20 strength. Instead of actually removing the lime it might be sufficient in many cases to convert it into a neutral and insoluble form, as, for instance, by the action of acid or neutral phosphates, oxalates, or arsenates. Some of the sulphonic acids of various coal-tar products have also been tried for the purpose with some success; and they are, at the same time, powerful antiseptics.

In the case of most light leathers where softness is aimed at, it is found necessary to use, either alone or as a supplement to some process of removing the lime, a putrefactive or fermentive bate, which has the effect of reducing ('abateing') the plumpness of the hide, and at the same time of softening it by attacking the fibrous tissue, and especially the elastic fibres. Either an infusion of dung (pigeons', hens,' or dogs') called *bate* or *puer* (the latter probably having some connection with the French *puant*), or of bran (drench), and frequently both, are used successively. The effect seems due to the enzymes and amino-acids produced by the putrefactive organisms, but the problem was partially solved by Wood in England, and by Popp and Becker in Germany, who introduced an artificial puer under the name of 'erodin,' consisting of a suitable culture of selected bacteria and a dry powder which when dissolved in water formed a suitable nutritive fluid for their rapid multiplication.

Dr. Rohm, following up an experiment of Wood's, has, however, introduced under the name of 'Oropon,' a mixture of ammonium chloride with a small quantity of the pancreatic ferment, which, for many leathers, has been very successful; though for the finest leathers, such as glove-kid, it has not completely superseded dog-puer. The exact degree of hydroxyl concentration of a solution has an important influence.

In the preparation of 'shaved' and 'dressing' hides, a bate may contain about 1 peck of hen or pigeon dung to 25 or 30 hides, in which they are handled frequently for 3–7 days. This time may be much shortened by warming the bate and working the goods with a drum or paddle tumbler. The latter consists of a tank or pit, generally having a curved bottom to favour the motion of the liquid, and agitated by a paddle-wheel with 6–8 floats. A short 'stocking' out of the bate was formerly sometimes employed. Tumbling with warm water with a limited quantity of dilute acid before bateing will wash out a good deal of lime and reduce the plumpness, and so save both time and material, but the skin must remain in a slightly alkaline condition; and French tanners make excellent shaved hides and calf-skins without bateing by careful working at the beam, long washing with cold water (during which probably a slight putrefactive action takes place), and the use of weak and stale liquors. Shaved hides are so called because, after the bateing, the thicker parts of the butt are reduced by shaving on an upright beam with a currier's knife having a turned edge.

Still lighter and more flexible sorts of leather, such as morocco and kid, are still often puered with fermented dog-dung, infused in hot water, and strained through a basket. This is frequently followed, after scudding, by a drench made by pouring boiling water on bran, and allowing to ferment. In this case, lactic acid is the most active product, although its plumping action is controlled by some putrefactive fermentation going on at the same time. Wood (J. Soc. Chem. Ind. 9, 27) has shown that starch is destroyed by the active ferment, and considerable quantities of methane evolved. In hot and thundery weather the lactic ferment is liable to be replaced by some other product, when the skins plump rapidly and become transparent, and are finally perforated or dissolved. The best precautions are to scald out the tubs thoroughly, and to wash the bran before using with cold water to remove the flour, which furnishes the nourishment required by the ferment.

In the brief space available it is impossible to give more detail as to these preparatory processes, which are, however, of the first importance from a practical point of view. From the scientific aspect, it must be noted that the plumping and 'falling' which the fibrous tissue suffers through the action of various reagents, is the result of osmotic pressure, and is at least as much a physical as a chemical phenomenon.

Tanning materials. Before speaking of the actual tanning process, a few words must be said about the chemistry of the vegetable products on which the operation depends.

The tannins, or tannic acids, are widely distributed through the vegetable kingdom, and form a large and varied class, differing considerably in chemical constitution as well as in properties. The one point which they all have in common is the power of precipitating gelatin from its solution as an insoluble compound. They are also all derivatives of the aromatic series of carbon compounds, and, so far as is known, all contain either pyrocatechol $C_6H_4(OH)_2$ or pyrogallol $C_6H_3(OH)_3$, and sometimes the isomeride of the latter, phloroglucinol. This difference usually corresponds to well-marked differences in constitution and properties. As a rule, the pyrogallol tannins give a blue-black with ferric salts, and a whitish deposit on the surface of the leather, well known to the tanner as 'bloom'; whilst the pyrocatechol derivatives give a greenish-black, and deposit red insoluble matters, oxides or anhydrides of the tannins. All catechol tannins give insoluble precipitates with bromine water, and with formaldehyde in presence of hydrochloric acid. Oak bark occupies an intermediate position, yielding both bloom and reds, and apparently containing both pyrogallol and pyrocatechol. In such cases, however, it is not very certain whether we have to deal with a complicated tannin or with a mixture of two dissimilar ones, since tannins, being neither crystallisable nor volatile, are very difficult to separate. It is known that many of the bloom-yielding materials, such as myrobalans, contain gallotannic acid, which yields no bloom, and ellagitannic acid, which yields a copious bloom of ellagic acid.

It is, of course, only the pyrogallol tannins which yield gallic acid as a decomposition product, while the pyrocatechol tannins contain the corresponding protocatechuic acid. Many of the pyrogallol tannins yield glucose on decomposition, but in the pyrocatechol class it seems to be absent.

A complete list of tannin-yielding plants would embrace a large part of the vegetable kingdom, but the following are those in most extensive practical use. (*Cf.* art. TANNINS.)

Oak bark is one of the oldest and best of tanning materials, producing excellent but not heavy leather; and, from its comparative weakness in tannin (8–12 p.c.) its action is somewhat slow. It yields a good deal of whitish bloom.

Valonia, the acorn cup of the *Quercus Ægilops* (Linn.) and *Q. Macrolepis* (Kotschy), contains up to 35 p.c. of a tannin somewhat similar to that of oak bark, but giving more bloom and a darker colour, and at the same time a heavier leather.

Myrobalans, the fruit of *Terminalia Chebula* (Ratz.) (India), contains 25–35 p.c. of gallotannic and ellagitannic acids, and, consequently, blooms freely It gives good colour and fair weight, and though alone it yields a porous and soft leather, it is very useful in mixture with dark-coloured materials, such as mangrove or mimosa extracts, for sole leather, and as a cheaper substitute for sumach, on the lighter descriptions.

Divi-divi, pod of *Cæsalpinia coriaria* (Willd.) (S. America), contains 30–50 p.c of a tannin somewhat similar in effect to that of valonia. It produces a heavy-weighing leather, but is dangerously liable to a sudden fermentation, which produces a deep red stain on all leather in contact with it.

Sumach, the pulverised leaves of *Rhus Coriaria* (Linn.), &c. (Sicily), yields 20–30 p.c. of tannins very similar to those of myrobalans, but paler in colour. It is principally used for light leathers, though warm sumach liquor is used to brighten the colour of heavy tannages There are also several American species used for tanning.

Mimosa bark, the product of several species of *Acacia*, principally Australian, but naturalised and largely cultivated in Natal, contains 20–40 p.c. of a red tannin derived from pyrocatechol, and yielding no bloom, but giving considerable weight and firmness to the leather. An extract has recently been introduced into commerce. Babool bark from *Acacia arabica* (Willd.) is one of the principal tanning materials of India (*A. Catechu* (Willd.) and *A. Catechu* var. *Sundra*, see below).

Cassia auriculata (Linn.), Turwad, avaram, or Tanghadi bark, from a leguminous bush allied to senna, is the principal tanning material for sheep and goat skins (so called 'persians') in Southern India.

Hemlock bark, known in this country principally in the form of extract, is produced by the hemlock pine, *Tsuga* [*Abies*] *Canadensis*, (Carr.) of North America. The bark contains 8–10 p.c., and the extract 20–30 p.c. of a tannin similar to that of mimosa, but giving a larger proportion of red anhydrides, and consequently a heavier leather, but at the same time one of a still more pronounced colour, which is less easily modified by other agents. It is the staple tanning agent of North America.

Gambier (*Terra Japonica*), pale catechu, an inspissated extract from the leaves of *Uncaria Gambier* (Roxb.) of the East Indies, contains 30–40 p.c. of a peculiar catechol tannin, which penetrates leather somewhat slowly, but has less astringency and adhesion to the hide fibre than most other tannins. These properties, which are apparently due to its large percentage of non-tanning matters, make it very valuable in certain stages of the tanning process, although alone it produces a leather of very inferior quality. Cutch (dark catechu), though somewhat similar in its chemical relations, is a very different product practically, and is derived from the wood of *Acacia Catechu* (Willd.) and *A. Catechu* var. *Sundra*, and, consequently, more allied to the mimosa bark, which has already been described. Gambier comes to this country in blocks of about 2 cwt., covered with mat and pasty in the centre, and also in cubes of about an inch square, which are much purer, and internally are quite white with crystals of catechin. Cutch comes in masses of a glossy dark brown fracture, and is principally used for dyeing.

Quebracho wood from *Quebrachia Lorentzii*, (Griseb.), a large tree of South America, and especially of the Argentine Republic, contains about 20 p.c. of rather difficultly soluble catechol tannin, principally used as extracts which are often decolorised and rendered soluble with bisulphites.

Mangrove barks from various species of *Ceriops* and *Rhizophora*. Extracts principally manufactured in East Indies. Barks vary a good deal in strength but may contain up to 40 p.c. of a dark red but fairly soluble catechol tannin.

Mallet bark from *Eucalyptus occidentalis* (Endl.) or 'flat-topped yate' of Western Australia. Rich in a brown catechol tannin producing rather hard leather if used alone.

Ulmo bark, said to be from *Euconpia cordifolia* (Cav.) of Chile, produces a dark red extract strongly resembling mangrove.

Artificial tannins.—Although none of the natural tannins can be synthesised, at least at commercial prices, a series of organic compounds have been produced which possess many of their properties, and some of which have come into considerable use in the production of leather. The first and most important of these were the 'syntans' discovered by Dr Edmund Stiasny, which were produced by the condensation of the sulphonic acids of phenols with formaldehyde, which were patented by the Badische Anilin and Soda Geselschaft, and which have not only been largely manufactured in Germany, but, since the war, in England under license. The master Eng. Pats. are taken out in the name of J. Y. Johnson, the Badische Co.'s agent, and are 8511 and 8512, 1912, but a good many patents have been since taken for other means of preparing tanning compounds, some of them doubtless to protect or evade the original patents, but others possibly of commercial value. Success in the actual manufacture depends on many details not mentioned in the specification, and particularly on the proper adjustment of temperature. The original products are very acid, and require to be partially neutralised before they can be used in tanning. When of good quality they produce a soft and practically white leather, which will resist water, but is easily stripped by alkalies. They form a good preparation for tanning with vegetable materials, and have a great bleaching effect, not only on dark-coloured vegetable tannages but on one-bath chrome leather, which may be made nearly white, and are largely used for this purpose. They precipitate gelatine and give blue-blacks with iron salts, and, like the lignine products, contained in sulphite wood pulp liquors, are precipitated by aniline and hydrochloric acid.

Exhaustion of tanning materials.—Most tanning materials require to be ground before lixiviating. This is accomplished either by a mill, on the principle of the ordinary coffee mill, with grooved iron or steel cones, or by one of the numerous forms of 'disintegrator,' in which the grinding is done by dashing the material against a serrated or grated casing, by beaters revolving 2000 or 3000 times a minute. Valonia and myrobalans are frequently crushed between fluted or toothed steel rollers. The grinding should not be so fine as to render percolation difficult. The actual exhaustion takes place in this country mostly in large square sunken vats, constructed like the other pits of the tannery and worked in series, the liquors being either pumped from one to the other or allowed to run by gravitation through wooden boxes, connecting the space below the perforated 'false bottom' of one pit with the top of the next. In America the 'leaches,' as the extracting vessels are called, are usually immense circular tubs, fitted with perforated 'false bottoms' and heated by steam coils. These are generally employed in groups of 6 or 8, water or weak liquor being run on the most nearly exhausted, and forced or pumped round the series to the newest and strongest vat. Hot extraction is more rapid than cold, and usually more complete, but the liquor is darker in colour, and contains more non-tanning matters, and the question of temperature must be decided by the particular material and conditions, some tannins being decomposed at temperatures which are not injurious to others.[1]

Tanning extracts now form an important portion of the materials used by the tanner, and in many cases render available materials which from their bulk and low percentage, or their remote origin, would not pay for transit, or yield sufficiently concentrated liquors for modern requirements. Among those of leading importance may be mentioned those of the woods of oak, chestnut, and quebracho, and of the barks of mangrove and hemlock pine. Valonia, myrobalans, and sumach are also extracted. The materials are prepared and extracted as above described, woods being previously reduced to chips or shavings by machines similar to those employed for dyewoods, and heat, occasionally under pressure, being freely used in extraction, especially with the weaker materials, such as oakwood, which only contains 2–3 p.c. of tannin. When this is done, decolorising methods are frequently employed to remove the dark and difficultly soluble matters dissolved by heating; the most approved method being partial precipitation by blood or blood-albumen, dissolved in the warm infusion, which is then heated beyond the coagulation temperature. Metallic precipitants are also sometimes used, and sulphurous acid and bisulphites, not merely as bleaching agents, but to render the phlobaphenes and 'reds' more soluble. A so-called 'pinewood extract' is on the market, made by concentration of the sulphite liquors of cellulose manufacture, which analyses well, but contains no true tannin and is used mainly as an adulterant; though it is absorbed by hide and probably has legitimate uses as a filling agent for sole-leather. After settling or filtering the decolorised liquors, they are concentrated in the vacuum pan to 50–60 p.c. of water for liquid extracts and 20–25 p.c. for those intended to solidify, spray-evaporators being largely used for concentration up to about 20 Bé.

Imperfect exhaustion is one of the most serious sources of waste in tanning, and the residues deserve more careful testing than is usually given to them.

Quantitative determination of tannins.—Many methods have been proposed for the purpose, several of which are capable of application under special conditions, but the only two that have stood the test of general practical work, and are both valuable for different purposes, are the hide-powder method, which is the gradual development of the work of several chemists, among whom Simand may be specially mentioned, and the permanganate and indigo process of Löwenthal.

The first of these permits an actual gravimetric determination of the matters absorbable by hide, but these include colouring matters, acids, and other substances not strictly tannins. It has been found that the absorption of these matters is lessened by a slight preliminary chroming of the hide-powder, and it must also be remembered that the method is purely empirical, and must therefore be carried out with absolute adherence to the smallest details if comparable results are to be obtained.

The following is the method of the International Association of Leather Trades Chemists, which is the official standard in Europe and only differs in minor details from that of the American Leather Chemists' Association; but a commission of the Society of Leather Trades Chemists has recently been appointed, who are working for its improvement. Its weakest points are the large proportion of non-tannins absorbed even by chromed hide-powder, and the uncertainty of the so-called 'insoluble matter,' largely consisting of difficultly soluble tannins, which will be removed by filtration. It is not improbable that the use of the Berkefeld 'candle' will be abandoned.

Preparation of infusion.—Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 grams of tanning matter per litre, and not less than 3·5 or more than 4·5 grams. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature of 17·5°, after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with. Sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials previously ground till they will pass through a sieve of 5 wires per centimetre, are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50° and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is desirable to allow the material to soak for some hours before commencing the percolation which should occupy not less than 3 hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as 'difficultly soluble' substances. The volume of liquid in the flask must be made up accurately to 1 litre after cooling

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[1] J. Soc. Chem. Ind. 1895, 635; 1898, 116.

The *total solids* must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution, at a temperature between 98·5° and 100° in shallow flat-bottomed basins, which shall afterwards be dried till constant at the same temperature, and cooled before weighing for not less than 20 minutes in an air-tight desiccator over dry calcium chloride *Moisture* is the difference between 100 and the percentage of total solids, and *insolubles* the difference between the *total solids* and *total solubles*.

Filtration.—The infusion shall be filtered till optically clear (see below) No correction for absorption is needed for the Berkefeld candle, or for S & S. 590 paper if a sufficient quantity (250 300 c.c.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed the average correction necessary must be determined in the following manner. About 500 c c. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 c c. is evaporated to determine 'total soluble No 1.' The remainder is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible), and 50 c c is evaporated to determine 'total soluble No 2' The difference between No. 1 and No 2 is the correction sought, which must be added to the weight of the total solubles found in analysis An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c c. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

(NOTE.—It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. & S. 605, 150 c c. being rejected, to about 5 mgr. per 50 c.c and where 2 grams of kaolin are employed in addition to 7½ mgr. The kaolin must be previously washed with 75 c c. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.)

The *total solubles* must be determined by the evaporation of a measured quantity of the solution previously filtered till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker placed in a good light on black glass or black glazed paper must appear dark and free from opalescence when viewed from above.

Hide-powder shall be of woolly texture, thoroughly delimed, preferably with hydrochloric acid, and shall not require more than 5 c.c. or less than 2·5 c.c of N/10 NaOH or KOH to produce a permanent pink with phenolphthalein on 6½ grams of the dry powder suspended in water. If the acidity does not fall within these limits, it must be corrected by soaking the powder before chroming for 20 minutes in 10–12 times its weight of water to which the requisite calculated quantity of standard alkali or acid has been added. The hide-powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70–75 p c. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgr per 100 c.c. The powder when sent out from the makers shall not contain more than 12 p.c. of moisture, and shall be sent out in air-tight tins.

The detannisation shall be carried out in the following manner.

The moisture in the air-dried powder is determined and the quantity equal to 6·5 grams actual dry hide powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and moistened with approximately ten times its weight of distilled water[1] 0·2 gram per hundred of dry powder of crystallised chromic chloride $CrCl_3,6H_2O$[2] is now dissolved in water and made basic with 0·6 gram Na_2CO_3 by the gradual addition of 11·25 c.c. of N/1 solution, thus making the salt correspond to the formula $Cr_2Cl_3(OH)_3$. This solution is added to the powder and the whole churned slowly for 1 hour. In laboratories when analyses are frequently made it is more convenient to use a 10 p c. stock solution, made by dissolving 100 grams of $CrCl_3,6H_2O$ in a little distilled water in a litre flask, and very slowly adding a solution containing 30 grams of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution, 20 c.c. per 100 grams or 1·3 c.c. per 6·5 grams of dry powder should be used.[3]

At the end of one hour, the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed repeatedly with distilled water, until on adding to 50 c.c. of the filtrate, 1 drop of 10 p.c. K_2CrO_4 and 4 drops N/10 $AgNO_3$, a brick-red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0·001 gram of NaCl in 50 c.c.

The powder is then squeezed to contain 70–75 p.c. water, and the whole weighed. The quantity Q containing 6·5 grams dry hide is thus found, weighed out and added immediately to 100 c.c. of the unfiltered tannin infusion along with (26 5–Q) of distilled water. The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute. It is then squeezed immediately through linen, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning until clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c or the residue of 50 c.c is multiplied by $\frac{6}{5}$. The non-tannin filtrate must give no turbidity with a drop of a 1 p.c. gelatin 10 p.c. salt solution.

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[1] Very woolly powders require slightly more than 10 times their weight of water A powder may be considered 'woolly' if it cannot be poured like sand from a beaker.—H.R P.

[2] 'Chrom-sesquichlorid cryst,' Kahlbaum. Satisfactory chromic chloride may now be obtained from the 'British Drug Houses'

[3] The solution sometimes changes colour slightly by keeping; but this has been shown to have no influence on results.—H R.P.

One gram of kaolin free from solubles must be used either by mixing it with the hide-powder in the shaking bottle or with the liquid before filtration.

All evaporations shall be rapidly conducted at steam temperature in shallow, flat-bottomed basins of not less than 6·5 cm. diameter to apparent dryness; and shall be subsequently dried between 98·5° and 100° in a water or steam oven until of constant weight, and shall be afterwards cooled in small air-tight desiccators over dry calcium chloride for at least 20 minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator. The residue is 'non-tannins.' The difference between these and 'total solubles,' is tanning matters.'

The Lowenthal method is volumetric, and, as very much weaker infusions can be employed, a larger quantity of water can be used in extraction, or it may be applied to very weak infusions without concentration It has gone out of use for commercial analysis, but the comparison of its results with the hide-powder method is sometimes useful in the detection of mixtures in extracts; and as a control method in tanning (*cp.* Procter and Hirst, J. Soc. Chem. Ind. 1909, 294).

The method depends on the oxidation of the tannin by permanganate in presence of excess of sulphonated indigo, which serves both as an indicator and regulator of the reaction.

The indigo solution is made by dissolving 5 grams of pure sodium or potassium indigo-sulphonate (Gehe's *Carminum cœrul. op.* answers well) in a litre of distilled water, adding 50 c.c. of concentrated sulphuric acid and filtering; or a solution of 1 gram 'Indigo pure B. A. S. F.' may be dissolved in 25 c.c. of concentrated sulphuric acid, and made up to 1 litre with water and a further 25 c.c. of acid. Samples which give a brownish instead of a pure yellow solution after oxidation are useless. The solutions keep well, but the weak permanganate is best made up as required, by diluting 100 c.c. of a 5 gram per litre solution to 1 litre.

The titration is best carried out in a beaker of 750–1000 c.c. capacity placed on a white tile; and if many titrations are to be made, should be provided with a screw-vaned stirrer driven by a turbine or other motor; but in any case the stirring must be vigorous and constant. 20–25 c.c. of the indigo solution, according to its strength, and 400 c.c. of good water free from organic impurity are introduced into the beaker, and permanganate solution is added from the burette as rapidly as it can be dropped until near the end-point. Uniformity in stirring and in the rate of dropping is of prime importance.

The colour changes first to green, and then to pure yellow, and as it approaches the latter, the flow must be checked and the last drops added very cautiously. The quantity of permanganate used will be that required to oxidise the indigo. If the process be now repeated with the addition of 5 c.c. of the tannin infusion, the excess required to destroy the blue will correspond to that required to oxidise the astringents added, and must not exceed two-thirds of that required for the indigo alone. A second estimation should not differ from the first by more than 0·1 c.c.; and the results added together will correspond to the total astringents in 10 c.c. of the infusion. But as gallic acid and other bodies always present in tanning materials are oxidised like tannin itself, it is necessary to make a second titration after removing the tannin, and estimate by loss. For this purpose hide powder, either white or chromed, may be used as in the previously described process, or to 50 c.c. of the liquor 25 c.c. of a fresh 2 p.c. gelatin solution and 25 c.c. of a saturated solution of salt containing 50 c.c. of concentrated sulphuric acid per litre. The mixture is shaken with a teaspoonful of kaolin for 15 minutes, filtered, and 10 c.c. titrated. The results of the gelatin method in the separation of gallic from gallotannic acid are nearly exact, but probably by a compensation of errors

As it is impossible to obtain *pure* tannins against which to standardise the results, which can only be compared with others obtained by a precisely similar mode of titration, pure recrystallised gallic acid has been found the most convenient and reliable standard, 5 c.c. of a freshly made solution of 0·1 gram per litre being titrated in place of the tannin solution. If it be desired to calculate from gallic acid to the results of the gravimetric method, the following figures may be employed, but it must be remembered that except in the case of gallotannic acid the comparison is not with a chemical individual, and the results only represent an average. 1 gram gallic acid = 1·34 gram gallotannic acid, 1·65 gram of the tanning matter of chestnut wood, 1·89 gram of that of oak wood, 1·73 gram of myrobalan, 1·69 gram of quebracho, and averaging all ordinary materials 1·76 gram. Further details are given by Procter and Hirst (*l.c.*).

Tannage of sole leather. As this is a simple and typical case of vegetable tanning it may be described in some detail. Knapp, in his classical essay on the Nature and Methods of Tanning (Natur und Wesen der Gerberei, Munich, 1858), adduces reasons for believing that leather is not an actual chemical combination of the gelatinous fibres of the hide with tannin, but rather that the action is a surface one in which they are coated with an insoluble matter which protects and makes them resistant to solvents and decay. Though this conclusion is not wholly true, it at least describes a reaction which is specially important in the case of sole leather. Whether the actual conversion of hide fibre into leather is the result of a strictly chemical combination, or of the formation of an adsorption compound, its solidification is certainly largely a case of surface-action. It has been said that both acids and alkalis swell the fibrous bundles and split them into finer fibrils, so offering a larger surface and more finely divided texture, and to produce a heavy and solid tannage it is found necessary that this should take place either before or during the tanning process. The English sole-leather tanner usually accomplishes it by the action of lime in depilation; the American, who unhairs by sweating, has to secure it by a separate treatment with sulphuric acid, while in other cases where sulphides or low liming are the agents of depilation, it is partly accomplished by these and partly by the organic acids present in the earlier tanning liquors. The avoidance of stale or old limes is important, as they plump badly and cause serious loss of weight, but sodium sulphide is useful as shortening the process. When a hide swollen with lime is brought into tanning liquors the weak acids present rapidly neutralise the alkali, and the hide, previously plump and firm, becomes soft and flaccid and falls in thickness. If little acid is present in proportion to tannin this action takes place very gradually, and the tannin penetrates rapidly in the alkaline state of the hide, but does not tan or fix the fibre, but when it is subsequently swollen by acids a plump rapid tannage is obtained, which, however, is often deficient in colour from the tendency of the lime to form tannates which darken in drying If, on the other hand, the hide, comparatively freed from lime, is brought into liquors where acid predominates over tannin, the tissue, at first soft and flaccid, swells gradually and combines with the tannin in an acid condition, again producing a plump leather and of good colour, since lime tannates are easily soluble in the acids present. But if, on the other hand, the unswollen hide comes into liquors which have insufficient acid to plump it, or if, having been swollen by lime, it is allowed to fall back as before described, the tannin will fix it in this fallen condition, and it will be impossible afterwards to plump it or to make thick leather.

(The free acid capable of dissolving lime tannate in a liquor is easily determined directly by adding saturated lime-water from a burette to a measured quantity of liquor, till it forms a permanent cloudiness; 10 c.c. of liquor should require from 5 to 15 c.c. Some of the acids which dissolve lime are too weak to produce any perceptible plumping effect on the pelt.)

For common sole and strap leather the first of these methods may be adopted with satisfactory results, though a previous deliming of the surface with weak solutions of boric, acetic, lactic, or some other weak acid is becoming increasingly common. If this is not done the hides or 'butts' (from which the bellies and shoulders have been trimmed in the beam-house) are simply suspended in limy water to remove the scud and loosely adhering lime, and are then brought into weak liquors, which have already lost most of their strength in previous use, and which may advantageously contain a considerable proportion of gambier, which has the property of colouring quickly without much contracting or drawing the grain. These liquors should be contained in deep pits in which the hides may be freely suspended, if possible without touching each other, and in which they may be kept in constant motion, at least for the first day, without exposure to the air, which would darken them by oxidising the alkaline tannates. This is best accomplished by suspension from frames to which an oscillating or traversing motion is given by power, but shaking frequently by hand will answer the same purpose. The butts or hides rapidly colour, and must be moved gradually forward into stronger liquors as the grain becomes set. It is difficult at this stage to state the suitable strength of liquor, since the specific gravity of these old liquors depends more on the impurities than on the tannin present, but they may range from 15° to 20° of the barkometer (sp.gr. 1·015–1·020) or even more in mixed tannage, and the liquor should contain no acids strong enough to redden methyl-orange, but should give a purplish-red to litmus paper.

If, on the other hand, it be desired to make a leather of first-rate colour and quality, the hides should be freed as perfectly as possible from lime by scudding and the use of some of the other methods already mentioned, and should come into weak liquors of oak bark, gambier, or other bright-coloured materials, which must contain a sufficient proportion of free acid to prevent entirely the rapid coloration which has been mentioned; the butts should colour much more slowly and then take rather a brown than an orange tint. This acidity may be obtained by using in the later parts of the process such materials as ferment and produce acetic and other acids, as for instance light oak bark and myrobalans, but it will sometimes be difficult to secure sufficient without the direct addition of acetic or other vegetable acid. Mineral acids, such as sulphuric and hydrochloric, must be avoided; but formic, butyric, and lactic acids are suitable, and oxalic acid may be used in small quantities to remove lime and to liberate the natural acids with which it was combined The goods must gradually be moved into stronger liquors, but care must be taken throughout to keep the acid in excess of the tannin, so that the butts gradually plump up and remain plump, and it must be borne in mind that so far as swelling is concerned, acid and tannin are antagonistic. Putrid or stale liquors (which are often styled 'sour' but contain little or no acid) must be sedulously avoided in every sort of sole-leather tanning. The great importance of the exact 'true acidity' (H ion concentration) is more and more recognised.

In the American treatment of 'acid' sweat-leather the sides are usually slightly coloured before plumping in a sweet and moderately strong hemlock liquor, and very dilute sulphuric acid used with water only, but if the colouring and plumping are done together, a sweet fresh hemlock liquor is used with the vitriol so as to tan the grain before it is much affected by the acid. The butts receive all their plumping in this acid vat, and are then tanned in liquors which contain no vitriol. Good results are not usually attained by adding vitriol in small quantities to the 'handler liquors.'

After the colour is fully set, and the butts by whatever method are fairly plumped in the suspenders, the rest of the process is very simple. The butts are laid flat in 'handler' pits, generally with liquor only, but sometimes with a little solid dusting material as the butts get forward. In these pits the goods are handled once a day or oftener, and the liquors are constantly changed and strengthened. This (or in the early layers) is the stage in which hemlock and other dark-coloured materials can be introduced with least injurious effect. Instead of this pit-tannage in the middle stage, drumming with much stronger liquors comes more and more into use, greatly shortening the time required, though possibly with some loss of quality: for which reason it is generally used as a secret process. When the butts are coloured quite through, they are placed in 'layers,' with stronger liquor and solid tanning material, such as mimosa bark, myrobalans, and valonia, strewed between them, and they are allowed to remain undisturbed for periods of from 1 to 6 weeks, according to the age and character of the goods and the practice of the tanner. This is repeated till the goods are fully tanned, when they are raised and drained, or sometimes washed from adhering 'dust' and strong liquor in a warm sumach or myrobalans liquor, or are 'vatted.' This process consists in suspension in a strong liquor made with bisulphited or 'bleaching' extract, or, preferably with neradol D (one of Stiasny's 'syntans'). They are then taken up into the drying lofts, where they customarily receive a slight oiling and are hung up until about half dry. They are then laid in a pile to soften and equalise the moisture ('sammed'), and the grain is struck out either by hand with the 'pin' (a two-handled knife with a triangular blade), or more generally by machine; again slightly oiled, somewhat further dried, and rolled twice and finally dried off in a warm loft. The exact dryness or 'temper' for the different operations is a matter of great importance, but is not easy to describe in writing, and it is besides somewhat influenced by the tannage. It is not uncommon to improve the colour of the grain by washing it with an aniline or other colour in the interval between striking and rolling 'off.' In place of 'striking' simple rolling with a rolling machine is coming more and more into use.

Dressing leather. Hides intended for 'shaved' hides are generally light, not exceeding 60 lbs. in raw weight; those for 'dressing' or 'common' hides may be somewhat heavier. They are unhaired with lime and bated with hen or pigeon dung, and 'shaved' hides are shaved over the thick parts of the butt with a currier's knife, the edge of which is turned in a peculiar way, and sharpened with a slender steel. They are coloured by frequent handling, or better by the use of a vat agitated by a rotatory paddle wheel, in a sweet liquor sufficiently strong to colour and set the grain in a distended condition, so that, as the inner portions swell in thickness and shrink in area from the weak acidity of the liquors, it becomes wrinkled up into a network of fine furrows. At this stage hides are often split with a reciprocating knife machine into 'grains,' which are finished in various ways, and 'fleshes,' which when good are usually 'waxed.' After this the tannage is conducted similarly to that of sole leather, but with much weaker liquors and tanning materials, selected to produce a soft and pliable leather. Any considerable acidity of the liquors which would swell the hide and produce a hard leather must be carefully avoided, while stale and so-called 'sour' liquors will soften and supplement the action of the bate, of course at the cost of a further loss of weight and firmness. In the shed, dressing hides are simply oiled and dried, but it is now more general to curry them wet out of the pits, an operation which is rather mechanical than chemical, but which consists in scouring out the bloom or deposit of ellagic acid which has formed in the surface, shaving down, and treating with oil and tallow. The 'stuffing' or impregnation with fats may be done by coating the moistened leather on one or both sides with 'dubbing,' a pasty mixture of tallow and oil of which the more liquid part is slowly absorbed; but it is now more usual to place the moistened leather in a warmed rotating drum, and run in the melted fats, which are absorbed in about 20 minutes. The mechanical processes are now almost entirely done by machines.

Enamelled, patent, or japanned leather. These names are applied to the various kinds of leather which are finished with a bright waterproof surface similar to the lacquered work of the Japanese, the first generally denoting leather so finished on the grain side, and with a grained surface. The colour is commonly, but not invariably, black. The leather may be tanned with a variety of materials, but must be well scoured and curried with but little oil or degras, and it is necessary that the hides should be well freed from grease by careful scudding before tanning, and now usually by the use of petroleum spirit or other solvents in a suitable apparatus. The skins are stretched on boards or frames, and coated with a linseed oil varnish boiled with Prussian blue, and sometimes lampblack, and other pigments. The colour of the japan is not blue, but a brown-black, and the iron of the Prussian blue acts not only as a colouring matter, but as a drier. The frames are then slid into grooves in a sort of closet heated by steam to 40°–60°, and when the coat is dry the process is repeated till the requisite thickness is obtained, each coat being smoothed with pumice before applying the next. In France and Germany the japan is frequently finally hardened in the sun, and ultraviolet rays from the mercury lamp have been successfully used for the same purpose. The American tanners are particularly skilful in treating large thin hides in this way. They are divided by the splitting machine into several thicknesses, and both the grain and flesh splits are frequently enamelled, the flesh split receiving a preliminary coating of thick boiled linseed oil and turpentine to form a sort of artificial grain. In recent times nitrocellulose solutions have been largely used to replace the whole or a part of the linseed oil composition.

Morocco, when genuine, is produced from goat-skins, but an article of equal quality is made from the rough-haired or 'blue-back' seal, and an inferior description, called 'French morocco,' from sheep-skins. The skins are unhaired by liming, puered with dog-dung, and passed through a bran drench, and are tanned with sumach, first in paddle-tumblers, and then in handlers. With sheep-skins the process is frequently much hastened by sewing them into bags, which are filled with sumach liquor and a little air, and are floated in a sumach bath and then laid on a shelf to drain and press. After a day's treatment they are again filled with a fresh sumach liquor, and this is usually sufficient to complete the tannage. When dried, these are called 'crust-roans.' The dyeing is done either by brushing on a table, or by folding down the back, or pairing, so as to protect the flesh side as much as possible, and drawing through a dye-bath, which is generally of aniline colours or dye-woods. In more recent times the natural have been almost entirely superseded by artificial (coal-tar) colours, and the dyeing is frequently done in a paddle vat or in a drum. The grain receives a slight glaze of albumen and is polished by glazing machines by friction under agate, glass, or hard wood, and is sometimes impressed with an artificial grain by engraved or electrotyped rollers; the grain being afterwards raised or improved by the operation known as 'boarding.'

Russia leather is tanned with willow, birch, and probably other barks, and is dyed with Brazil wood grounded with stannic chloride. Its peculiar odour is due to the essential oil of birch-bark tar, which is applied during the finishing process. Many imitations made in England and on the Continent are scented by a small proportion of this, applied mixed with oil, to the flesh-side.

'Chamois' or **wash-leather** is a totally different product from those which have been already described The ordinary article is made from the flesh-splits of sheep-skins, and is thoroughly limed so as to dissolve as much as possible of the cementing substance of the fibres, and so produce softness. The lime is then removed by a short bran-drench, and after the superfluous moisture has been pressed out, the skins are oiled on a table with fish or whale oil, folded in cushions, and worked under fulling stocks for 2 to 3 hours, and then shaken out and hung up for a short time to cool and partially dry. (In England the oil is usually gradually added during stocking) The process is repeated again and again until the water has been entirely replaced by oil, and they are then laid in a pile in a warm place, when a sort of fermentation takes place with a considerable production of heat caused by the oxidation of the oil, and the skins take a yellow colour. The surplus oil is now removed either by pressure ('degras') or by washing with potash or soda lye, from which 'sod oil' is recovered by neutralisation with sulphuric acid. Though it is not known what chemical change takes place in the fibres, the leather is extraordinarily resistant both to boiling water, acids, and alkalis, and yields no gelatin on boiling. It has been supposed that the fibres were merely coated with oxidised oil-products, but this is negatived by the fact that the leather is unaffected by alkalis which readily dissolve oxidised oils, and it is more probable that the tannage is due to aldehydic products of the fatty acids and glycerol. Only oils of which the fatty acids have unsaturated double bonds will produce the result, and the most unsaturated are the most effective. Excellent leathers of a chamois type are produced by direct treatment with formaldehyde and some other aldehydes in a solution rendered alkaline by sodium carbonate (Payne and Pullmann's patent, 2872, 1898).

Crown leather (Preller's, or **Helvetia leather).** This leather, which is remarkable for its toughness, may be regarded chemically as intermediate between 'chamois' and kid, as it is produced by the action of oils and fats in conjunction with an albuminous 'filling' quite analogous to the egg-yolks and flour which are used in the kid manufacture. As the leather is employed for belting, picker straps, and other mechanical purposes, well-flayed hides of medium substance are most suitable. They are unhaired by sulphides or sweating, or by a very short liming hastened by mechanical motion, so as to lessen injury to the fibre. For the sake of appearance they are often grained and coloured by working for 1–2 hours in a paddle tumbler in a moderately strong chestnut, hemlock, or other tanning liquor. They are then swollen (if not unhaired with lime), by paddling for a few hours with about 3½ oz. of sulphuric acid per hide, washed through clean water, and hung up until half dry. They are next spread on a table and covered on the flesh with a layer of tanning paste ¼ inch thick. This may be composed of 7 parts wheat flour, 7 parts horse grease, 1 part salt, and 1–2 parts tallow. (Originally ox-brains were used in the mixture, but are not necessary.) They are then folded in bundles and are placed in a large drum studded with pegs inside, and warmed by the injection of moist air to about 30° or 40°, according to the hardness of the fats employed, in which they are worked for 8–12 hours; at the end of this time they are again partially dried and coated with the fat-mixture, and the process repeated four or five times. The hides are then washed in water, and sometimes with a little soda, and are curried by setting out on both sides, and boarding to raise the grain. The yield is only about 30–40 p.c. of the raw weight of hide.

Calf- and glove-kid. As it is impossible within the limits of this article to give working details where the greatest nicety is required in every stage of manufacture, and as the general outlines are the same in both these products, it must suffice to take them together, briefly indicating how the different qualities of each are produced; especially as calf-kid has been almost entirely superseded for shoe purposes by chrome leathers In calf-kid considerable firmness is required, together with great pliability, whilst in glove-kid, which is made from actual kid-skins, as well as to a large extent from fine lamb-skins, not only the greatest softness, but the property of stretching in every direction without tendency to spring back, is essential. This characteristic difference is due partly to the different character of the skins employed, and to the fact that in the latter case special care is taken in the beam-house so to dissolve the cementing matter of the tissue that the separate fibres can move over each other without adherence. Hence the calf-skins are usually unhaired simply by a rather thorough liming, whilst the kids are treated with limes which, in addition, contain realgar (red sulphide of arsenic), which is mixed with the hot slaked lime. In each case the skin is scoured, first with a bate of dogs' dung, and then with a bran drench; and in both cases, but especially in the latter, the washing and working on the beam is very thorough, since unless the fat-glands and scud are very completely got rid of, it is impossible to dye the skins uniformly and properly. The tannage is effected in a drum containing a mixture of flour, alum, salt, and egg-yolks, with an addition of olive oil, being in principle a combination of mineral tannage with that of oil and albumen as described under 'crown leather.' After tanning, the goods, whether for shoe or glove purposes, are dried, softened by 'staking' or drawing over a blunt knife, and 'aged' by keeping at least a few weeks in a cool warehouse to fix the tan. Calf-kid is then damped and shaved on the flesh, and dyed black after grounding with a mixture of stale urine, or ammonia and potassium dichromate with logwood, sometimes by brushing, and sometimes by folding grain side out, and passing through a bath of the dye-liquor, and the dye darkened and fixed by a wash of ferrous sulphate. The skins are then re-egged to restore the egg, &c., removed in washing and dyeing, partially dried, and then grounded with a moon-knife (a round knife with a central handle), rubbed over the grain with a mixture of wax, soap, and gum, and ironed to give them a gloss, hand labour being almost entirely superseded by machines.

In glove-kid the dyeing process is much more complicated, and most of the tannage is washed out with warm water, which necessitates a second feeding in the drum with egg-yolk and salt. The colours are produced by a great variety of dyes and mordants, among which the juices of a variety of berries may be mentioned. Aniline dyes are rarely used alone, but are frequently employed as a final wash to brighten the colour. After dyeing, the skins are wrung out or 'sleeked' out with a brass or vulcanite sleeker on a beam, dried, and again slightly damped and stretched by drawing over a blunt knife which is fixed on a post; an operation which is called 'staking.'

Mineral tanned leather. It has long been known that not only aluminium salts, but those of iron and chromium of corresponding type were capable of producing leather, and as early as 1858, Knapp described a method of chrome tanning, which is identical with one of the modern processes; but it is only within recent years that it has been realised that such leathers possess valuable properties, and especially as regards their resistance both to hot and cold water, which justify the much greater expense of chrome as compared with aluminium salts. It is quite possible to produce chrome leathers with chrome alum and salt, but practically Knapp's suggestion of forming a basic salt either by addition of sodium carbonate to the solution or in some other way is always employed in 'one-bath' tannage; while the 'two-bath' process of August Schultz, which curiously came into practical use before that of Knapp, actually produced a basic salt in the skin, by treatment with chromic acid and its subsequent reduction with acidified sodium thiosulphate. In either case the salt in the skin afterwards is rendered still more basic by 'neutralisation' with dilute solutions of borax or some other weak alkaline salt, and the leather is afterwards 'fat liquored' with a thin emulsion of oil and soap, dyed, and subsequently dried out and softened by 'staking' by machine.

Iron leathers have never attained any commercial importance, although Knapp spent time and money in trying to develop them. Titanium and cerium salts have been shown to possess tanning properties, but are still in the experimental stage. Probably most salts which produce colloidal precipitates are capable of producing a sort of semi-mechanical tannage.

Investigations on chrome tannage have thrown much light on mineral tannages in general. It is now generally admitted that the salts are decomposed by hydrolysis, and the acid combining with one or more of the amino-groups to form a gelatine salt, and the less soluble basic ion adsorbed by the large surface of the separated fibrils. This adsorption is probably partly physical, but there is a good deal of evidence that a salt of chromium is finally formed with the gelatine carboxyl (A. and L. Lumière and Seyewitz, Bull. Soc. chim. 1903, iii, 29, 1077), containing 3·3-3·5 p.c. of Cr_2O_3 on the gelatine. Wilson also (J. Amer. Leather Chem. Assoc. 1917, 108; and Collegium (London) 1917, 105) gives strong reason to believe that an actual compound of about the same composition is formed with hide fibre, but there is no doubt that beyond this, considerable quantities of chrome oxide or a basic chrome salt may be fixed by adsorption. The gelatine compound is insoluble even in boiling water, but is decomposed by both acids and alkalis. Considerable doubt exists whether the so called basic solutions of chrome salts are really definite salts, colloidal solutions of chrome oxide in the normal salt, or salts of complex ions. Bassett (J. C. S. 1903, 692) shows that sulphuric acid contained in the solution produced by reduction of dichromates with SO_2 no longer reacts with barium chloride. For practical purposes the basicity is estimated by hot titration with NaOH, and compounds corresponding to $CrCl_2(OH)$ are found to be suitable for sole-leather tannage, while for the finer and softer leathers they are advantageously somewhat more basic. Hydroxy-acids form complex ions with Cr which do not tan, and a solution of sodium potassium tartrate (Rochelle salt) will remove the whole of the Cr from chrome leather, while almost the whole of the tartaric acid can be recovered by suitable acidification as acid potassium tartrate (Procter and Wilson, J. Soc. Chem. Ind. 1916, 156). Lamb has also patented the use of oxalic acid for the same purpose.

For the 'one-bath' process of tanning, basic solutions are invariably employed, though soft and lightly chromed leathers can be made with normal chrome salts by the addition of sufficient common salt, but the absorption of chrome is limited to the amount rendered basic by the absorption of acid by the amino-groups of the skin itself, and the salt is necessary to prevent excessive swelling. Knapp made his basic liquor by the addition of sodium carbonate to the normal salt, Martin Dennis by dissolving chromium hydroxide in hydrochloric acid, and adding soda if necessary; and liquors suggested by Procter have been largely used in which either chrome alum solution is rendered basic by soda or bichromate is reduced in presence of a calculated quantity of acid by sugar or glucose, for which other inventors have substituted starch and glycerine. Probably the best basic liquor is that recently suggested by Procter, but apparently already in use as a trade secret by certain firms, in which bichromate is reduced directly by gaseous sulphurous acid. If the reaction is complete the equation is

$$Na_2Cr_2O_7+3H_2SO_3 \\ =Na_2SO_4+Cr_2(SO_4)2OH+3(H_2O)$$

but it is certainly an equilibrium reaction, and *if* SO_2 *is present in large excess,* Bassett's equation

$$K_2Cr_2O_7+4H_2SO_3=K_2SO_3+Cr_2(SO_4)_3+4H_2O$$

is probably partly justified. Practically, however, as H_2SO_3 has little swelling action on the skin, the liquor acts as if the first equation were fulfilled, and gives the same results when titrated with soda. It is thus suitable for sole leather without any addition, but for light leathers should perhaps be made slightly more basic, when it has proved very successful even for chrome-kid. It tans very rapidly, completely tanning thick hide in still suspension within 48 hours. Sodium bichromate is better than the potassium salt, since its much greater solubility enables concentrated solutions (15–18 p.c.) to be made which can be diluted as required.

Single-bath tannage can be carried out either in suspension, or more rapidly in the paddle or drum. The hides or skins are prepared much as has been described for other tannages, and are treated with liquors of increasing strength, or often of slightly increasing basicity, or very successfully, simply by using fresh packs for exhausting the liquors previously used for more advanced goods, as in the case of vegetable tannage.

In Schultz's two-bath tannage the prepared skins are first treated in an acidified solution of a bichromate, about 5 p.c. of bichromate either of soda or potash and 2½ p.c. of hydrochloric acid, or an equivalent quantity of sulphuric, being used on the weight of wet skin. When the skins are thoroughly yellow throughout they are transferred to a bath containing 10 p.c. or more of acidified sodium thiosulphate, in which the skins become bluish-green and the actual tannage takes place. The chemistry of the reduction is very complex, and sulphur is deposited on the skin.

After tannage by either method, and subsequent washing, the skins are 'neutralised' or treated with a weak alkaline solution which renders the absorbed chrome salt more basic and less soluble, and prevents the curdling of the subsequent 'fat liquor.' A weak solution of borax is generally used, but a better method invented by Stiasny consists in the use of a solution containing 4 p.c. of ammonium sulphate and 4 p.c. of crystallised sodium carbonate, of which it is best to add only 2 p.c. at first, and the rest if required. With this solution, owing to the weakness of ammonia as an alkali, and the repressing effect on its ionisation of the excess of ammonium sulphate, it is impossible to over-neutralise, which may easily occur even with borax. The activity of the bath can be restored by the addition of further quantities of soda as required.

The skins are then drummed with a fat-liquor containing a small percentage of soap and emulsified oil, and are dyed, dried out, and finished. The dyeing must take place before drying, as it is impossible so to re-wet the skins as to enable them to absorb the dye. Logwood and iron is generally used for blacks, and acid dyes for colours, as the basic dyes can only be fixed by previous mordanting with tannin.

A skin properly chromed by either process should stand boiling in water without shrinking. 'Semi-chrome,' which is vegetable tannage partially stripped of tan by alkali and re-chromed, is not nearly so resistant.

H. R. P.

LEATHER BROWN-YELLOW, CHRYSANILINE, *v.* ACRIDINE DYESTUFFS.

LECANORIC ACID (*Diorsellinic acid*)

$$C_{16}H_{14}O_7,H_2O$$

was first described by Schunck under the name of 'lecanorin,' and was isolated by him from various species of the *Lecanora* and *Variolaria* lichens. It is also present in some quantity in the *Rocella canariensis*, *R. portentosa*, *R. sinensis*, and *Parmelia perlata* (*l.c.*), and, according to Hesse (Annalen, 139, 24), is best isolated by the following method, which is a modification of that originally devised by Schunck. The finely divided lichen is extracted with ether, the extract evaporated, and the greenish-white crystalline residue treated with lime water. The solution, when neutralised with acid, gives a precipitate of lecanoric acid, which is collected and crystallised from alcohol. In case the product is not quite pure it is treated with ether, which dissolves the acid, but not the impurity.

Lecanoric acid crystallises in colourless needles, m.p. 166° (Hesse, Ber. 37, 4693), the solutions of which possess an acid reaction. With alcoholic ferric chloride it gives a dark purple coloration, and with dilute calcium hypochlorite a blood-red liquid, which, according to Hesse, is characteristic, and can be used to distinguish this substance from the known lichen acids.

Dibromolecanoric acid (Hesse, Annalen, 139, 28) $C_{16}H_{12}O_7Br_2$ consists of minute prisms, m.p. 179°, whereas *tetrabromolecanoric acid* $C_{16}H_{10}O_7Br_4$, prisms, melts at 157°.

Potassium lecanorate $C_{16}H_{13}O_7K,H_2O$; *barium lecanorate* $(C_{16}H_{13}O_7)_2Ba,5H_2O$; *calcium lecanorate* $(C_{16}H_{13}O_7)_2Ca,4H_2O$; *silver lecanorate* $C_{16}H_{13}O_7Ag$; *lead lecanorate*

$$(C_{16}H_{13}O_7)_2Pb+PbH_2O_2$$

and *copper lecanorate* $(C_{16}H_{13}O_7)_2Cu,2H_2O$ have been obtained (J. pr. Chem. [ii.] 57, 264).

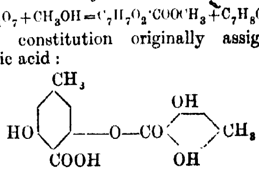
When boiled with water, lecanoric acid yields *orsellinic acid* $C_{16}H_{14}O_7+H_2O=2C_8H_8O_4$; whereas by means of boiling acetic acid or baryta water, orcin and carbon dioxide are simultaneously produced:

$$C_{16}H_{14}O_7+H_2O=C_8H_8O_4+CO_2+C_7H_8O_2$$

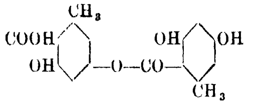
On the other hand, methyl alcohol at 85° gives, in addition to orcin and carbon dioxide, *orsellinic acid methyl ester*:

$$C_{16}H_{14}O_7+CH_3OH=C_7H_7O_2\cdot COOCH_3+C_7H_8O_2+CO_2$$

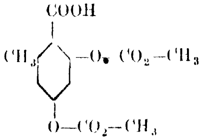
The constitution originally assigned to lecanoric acid:



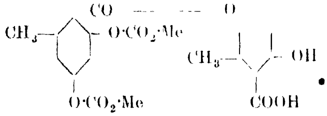
in view of the work of Heinrich (Ber. 37, 1406) on orsellinic acid, is more accurately expressed as follows:



This structure has been confirmed by the synthesis of the acid (Fischer and Fischer, Ber. 1913, 46, 1138). These authors converted *dimethyl-carbonato-orsellinic acid*:



into its chloride (m.p. 53°–56° C.) by the action of phosphorus pentachloride in presence of acetone, dissolved the product in the same solvent and gradually added a well-cooled solution of orsellinic acid in acetone and N aqueous sodium hydrate, whereby *dimethyl-carbonato-orsellinoyl-orsellinic acid*:



needles, m.p. 185°–187° C., was formed. When hydrolysed by means of aqueous caustic soda, this slowly passes into lecanoric acid, colourless needles, which softens at 170°, and is completely melted at 175°, with evolution of gas (*cf.* Hesse). The crystals when air-dried contain 1 molecule of water of crystallisation.

The identity of the product thus obtained with natural lecanoric acid was established by comparing their melting-points, colour reactions with ferric chloride, and with bleaching powder solution, and finally by converting each into *methyl-lecanorate-trimethyl-ether*, $C_{20}H_{22}O_7$.

The trimethyl-ether of methyl-lecanorate has been shown by Fischer (Ber. 1913, 46, 3253) to be identical with the product of the action of diazomethane on evernic acid.

A. G. P.

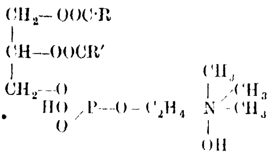
LECITHIN is a monaminomonophosphatide belonging to the group of phosphorus-containing fats known as 'lipins.' The occurrence of these complicated fats was first described by Fourcroy in 1793. Lecithin occurs in practically all animal tissues, and is intimately associated with the cell-protoplasm; indeed, it is necessary for this combination to be broken up, by treatment with alcohol or other means, before the whole of the lecithin can be extracted. The proportion of lecithin in the different tissues varies considerably; in dried ox-heart, 10 p.c. has been found; in egg-yolk, 9·5 p.c.; whilst in the spinal cord of the rabbit as much as 35 p.c. is present (Erlandsen, Zeitsch. physiol. Chem. 1907, 51, 71; Roaf and Edie, Thompson Yates Lab. Report, 1905, 201; Nerking, Biochem. Zeitsch. 1908, 10, 193). In human milk from 0·024 to 0·079 p.c. occurs; in plants, lecithin is present chiefly in the seeds. Schulze found the following proportions in leguminous plants: in beans, 0·30 p.c.; lupins, 0·37; vetches, 0·39; peas, 0·61 (Lands. Versuchstat. 1891, 269).

Preparation (MacLean, J Path. Bact. 1914, 490).—The tissue, which should be as fresh as possible, is minced and stirred up with several times its volume of acetone or alcohol; after standing, the solid is separated by filtration through a cloth, and pressed out in a laboratory hand-press. The cake remaining is dried at room temperature under an electric fan for half an hour and then ground in a coffee mill to a fine powder. The dried powder is shaken with excess of alcohol for from 2 to 3 hours and the alcoholic layer decanted. The process is repeated four to six times, the alcoholic extracts added together and concentrated at 40° under reduced pressure. The residue is taken up with a small volume of ether and excess of acetone added; the resulting precipitate is rubbed together with a pestle and separated, redissolved in ether, and the process repeated four or five times. The precipitate is then emulsified with water by rubbing it up in a mortar, and a little sodium chloride and half its volume of acetone added; the precipitate is filtered off through a finely-perforated filter-paper and re-emulsified and reprecipitated three times. After drying by acetone, it is taken up with ether, and centrifuged, the process being repeated until a precipitate completely soluble in ether is obtained. The substance is now dissolved in alcohol and any residue allowed to settle; the decanted liquid is then filtered and the alcohol evaporated at 40° under reduced pressure; the residue is dissolved in ether and precipitated by acetone, dried by several changes of acetone, and finally *in vacuó* over concentrated sulphuric acid.

The substance commercially known as lecithin is a mixture of the two phosphatides, lecithin and kephalin, in widely varying proportions according to its method of preparation. Partial purification may be made by extraction with alcohol, lecithin being soluble in this solvent, and kephalin, the other lipin present, insoluble. Ether, unless very carefully purified, tends to increase the amount of alcohol-insoluble substance present.

In preparing lecithin from yolk of egg, Bergell (Ber 1900, 2584) extracted the dried egg with 96 p.c. alcohol, and precipitated the mixture with an alcoholic solution of cadmium chloride at 0°; the lecithin cadmium chloride salt is suspended in alcohol, extracted with ether, and then boiled with eight times its volume of alcohol (80 p.c.) under a reflux condenser. The cadmium was removed by the addition of ammonium carbonate solution to the boiling alcoholic solution. The filtrate was cooled to −10° and the precipitate which separated was dissolved in chloroform, precipitated with acetone and dried *in vacuó* over sulphuric acid. The high percentage of choline found in certain commercial products is probably due to this method of preparation, as kephalin, the lipin which usually accompanies lecithin, forms a cadmium chloride salt soluble in alcohol and therefore not precipitated by the above method (*cf.* Lecithin, MacLean, Longmans & Co., p. 26).

Constitution.—Lecithin is represented by the formula:



$$\begin{array}{l} CH_2-OOC\cdot R \\ | \\ CH-OOCR' \\ | \\ CH_2-O \\ \quad HO\diagup P-O-C_2H_4-N(CH_3)_3 \\ \quad O \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad OH \end{array}$$

where R and R′ are fatty acids residues. The glycerol forms an ester with 2 molecules of fatty acid and with phosphoric acid, the latter being also combined with choline. Considerable discussion has taken place with regard to (1) the nature of the base; (2) the nature of the fatty acids; and (3) the structure of the glycerophosphoric acid and the nature of its combination with the choline.

(1) Strecker (Ann. 1862, 353) identified the base of lecithin as choline; the amount present in lecithin obtained from different sources varies largely. Unless special means of separation are used, preparations of lecithin contain varying proportions of a second lipin, kephalin. Lecithin contains choline as its base; in kephalin the choline is replaced by *β*-amino ethyl alcohol (Trier, Zeitsch physiol Chem. 1912, 76, 496; 1913, 86, 1; Eppler, *ibid.* 1913, 87, 233; MacLean, Biochem Zeitsch. 1913, 57, 132; Biochem. J. 1915, 351).

(2) Stearic, palmitic, oleic, and linolic acids have all been described as hydrolytic products of lecithin. The experiments have, however, been carried out with impure lecithin, and it is possible that the kephalin present is the source of the stearic and linolic acids and lecithin of the palmitic and oleic acids. The question is not finally settled (Cousin, Compt rend 1903, 68; J. Pharm. Chim. 1906, [vi.] 225; Serano and Palazzi, Chem. Zentr. 1911, [ii.] 772; Levene and Rolf, J. Biol. Chem. 1921, 46, 193, 353; Levene and Simms, *ibid.* 18, 185)

(3) The glycerophosphoric acid. Either the primary or secondary alcohol group of the glycerol might be esterified with the phosphoric acid, but only the ester of the secondary alcohol group would show optical activity. Bailly (Compt. rend. 1915, 160, 395) claims to have isolated both forms of glycerophosphoric acid from lecithin. The choline is regarded as combining with the glycerophosphoric acid through its alcoholic hydroxyl, an ester-like compound being obtained (Strecker, *l.c.*; Gilson, Zeitsch. physiol. Chem. 1888, 585).

Properties.—Lecithin is a yellowish waxy hygroscopic substance; soluble in almost all organic solvents except acetone and methyl acetate. Acetone precipitates it from alcoholic solution, especially in the presence of a small amount of sodium chloride. Lecithin combines with both acids and bases; it forms well-characterised addition compounds with cadmium, mercuric, and platinic chlorides. It forms compounds with proteins, and with carbohydrates, though it seems probable that the latter are not chemical entities but adsorption complexes. It is dextrorotatory; heated in a sealed tube at 100° for some time it becomes inactive. The lævo-form is left unaltered on treating the racemic form with lipase (Mayer, Biochem. Zeitsch. 1906, 1, 81; 1908, 8, 199). Lecithin is readily oxidised, and on standing in air becomes insoluble both in alcohol and in ether; the unsaturated fatty acids present are probably converted into hydroxylated derivatives, but other changes also take place. It should, therefore, be preserved *in vacuô* and in the dark. The presence of iron salts and the impurities present in commercial ether both catalyse the oxidation. Bromine and iodine are readily absorbed by the unoxidised substance (Riedel, D. R. P. 156110, 155629).

Biological properties.—Lecithin has been described as playing an important part in the phenomena of immunity. It is probable, however, that the great variety of the results obtained is due to the impurities accompanying the lecithin used in this work, and it is extremely doubtful whether pure lecithin has any antigenic function. Most of the work carried out on the biological action of lecithin has been done with impure material and is therefore of little value. It is said to act as a stimulating agent for growth (Desgrez and Zaky, Compt. rend. 1902, 1166, 1522; Hatai, Am. J. Physiol. 1904, 57). According to Overton (Studien uber die Narkose, 1901, Jena) the lipin cell-membrane plays an important part in regulating the exchange of substances between the cells of the animal organism and the surrounding medium. Vernon (Biochem. Zeitsch. 1912, 47, 374; 1913, 51, 1; 1914, 60, 202) has shown that lipins play an important part in the action of the cell oxidases, the latter being rapidly destroyed by first treating the cells with certain concentrations of organic solvents. From the extent and nature of their distribution it is certain that the function of lecithin in the organism is one of primary importance, but at present we do not know what it is. I. S. M.

LECITHINASE *v.* Snake venom.

LEDITANNIC ACID, LEDUM CAMPHOR *v.* Ledum palustre (Linn.).

LEDUM PALUSTRE (Linn.). *Marsh tea*; *Wild rosemary. Ledon* (Fr.); *Porsch, Sumpfporst* (Ger.); a shrub (N.O. *Ericaceæ*), some 3 feet in height, inhabiting marshes throughout the northern hemisphere. The leaves possess acrid narcotic properties, and were formerly made use of in medicine. A strong decoction is now sometimes applied in veterinary practice to destroy cutaneous parasites, and it is also employed to kill vermin in furniture. The plant has also been employed as a substitute for hops (Schmidt, Pharmaz. Chemie, 1911, [ii.] 2, 1857). The *volatile oil* obtained by distilling the leaves with water was examined by Willigk (Sitzungsber. Wien. 9, 305) and Fröhde (J. 1861, 692). Yield, 0·4–1 p.c.; $d^{15°}$ 0·932–0·963; reddish, viscid. It contains *acetic, butyric, valeric* acids, a *terpene* $C_{10}H_{16}$, boiling at 160°, an *oxygenated oil* $C_{10}H_{16}O$, perhaps *ericinol*, boiling at 240°–242°, and a camphor.

Ledum camphor $C_{15}H_{26}O$, was examined in 1796 by Rauchfuss (J. Pharm. 3, 1 and 189) and later by others, including Hjelt and Collan (Ber. 1882, 15, 2501). The camphor crystallises out abundantly when the volatile oil is placed in a freezing mixture, and may be separated and purified by recrystallisation from alcohol. It sublimes readily in needles, which melt at 104°–

05°, and boil at 282°–283°. The solution in ulphuric acid is coloured violet by a drop of itric acid Heated with acetic anhydride at 50° a sesquiterpene *ledene* $C_{15}H_{24}$ is obtained, which boils at 255°, and at 0° has a sp.gr. 0·9349 Hjelt, Ber. 28, 308) (*v.* CAMPHORS).

Marsh tea contains small quantities of the glucoside *ericolin* $C_{34}H_{56}O_{31}$ (?) (Rochleder and Schwarz, Sitzungsber. Wien. 9. 308; 11, 371) a compound which occurs generally in ericaceous plants (Kawalier, *ibid.* 9, 297; Thal, J. 1883, 1402). It is an intensely bitter, yellowish-brown, sticky resin (*v.* ERICOLIN). By the action of dilute acids it breaks up into glucose and *ericinol*, $C_{20}H_{26}O$ (?). The latter compound is also a product of the action of dilute acids on pinipicrin, a glucoside occurring in the needles of the fir and other conifers (Kawalier, Sitzungsber. Wien. 11, 350, 13, 515). Ericinol is a colourless oil when first obtained, but it soon oxidises and turns brown when exposed to the air.

Leditannic acid $C_{15}H_{20}O_8$ (?) was examined by Willigk (Sitzungsber. Wien. 9, 302), Rochleder and Schwarz (*ibid.* 9, 307), Rochleder (*ibid.* 44, 493), and Thal (J. 1883, 1402). Perhaps identical with the tannin of the horse-chestnut.

G. B.

LEEK. *Allium Porrum* (Linn.). The Welsh national plant. The taste and odour are due to the presence of allyl sulphide $(C_3H_5)_2S$.

Konig gives the following analyses:—

	Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash	Organic sulphur
Root and bulb	87·6	2·8	0·3	0·4	6·1	1·5	1·2	0·06
Leaves .	90·8	2·1	0·4	0·8	3·7	1·3	0·8	0·06

The following shows the composition of the ash:—

	Per cent of ash in dry substance	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Root and bulb	6·3	30·7	14·1	10·4	2·9	7·6	16·7	7·4	7·3	3·1
Leaves .	8·2	40·7	6·9	21·7	4·1	0·6	7·6	4·1	7·3	6·6

H. I.

LEGUMIN. *Vegetable casein* (*Phaseolin*). The distinctive protein of the seeds of the *Leguminosæ*, found also in some other seeds; it closely resembles in composition and in some of its properties the casein of milk. It occurs mixed with other proteins in the seeds, and is with difficulty obtained in a pure state.

Different methods of extraction—especially the use of dilute alkalis—cause alterations in the proteins of plants, and hence a good deal of confusion has arisen both as regards the nature and the names of the various proteins.

Legumin was discovered by Einhof in 1805, and has been investigated by Proust, Vogel, Boullay, Braconnot, Liebig, Dumas, and Cahours, and others, and especially by Ritthausen, and later by T. B. Osborne and his fellow-workers.

Ritthausen divided plant casein into legumin, conglutin, and gluten-casein, which differ a little from each other in their composition and in a few of their properties. The first and third he considered albuminates, and the second a plant globulin

These three forms of plant casein are, according to Ritthausen, only slightly soluble in water, but easily soluble in dilute alkaline solutions, in solutions of alkaline reacting salts, and in very dilute acids. They are precipitated from alkaline solutions by dilute acids and by rennet. Earlier investigators thought that phosphorus was an essential element. Sp.gr. 1·285–1·36 (Dittmar); specific rotation of legumin in 10 p.c. NaCl $[\alpha]_D - 44{\cdot}09°$ (Osborne and Harris).

Ritthausen obtained legumin from peas, haricots, beans, lentils, vetches, &c., by the following process. The seeds are finely powdered, macerated with about eight times their weight of cold water for 6 hours, the liquid decanted and strained, and the residue again macerated with water. In some cases, notably with beans and lupins, the solution is acid, and in such cases it is desirable to add to the water used in extracting the seed sufficient potassium hydroxide to render the mixture very feebly alkaline, otherwise much less proteid will be extracted from the seed. The strained extract is allowed to settle for some time at a low temperature, 4°, and when clear, or nearly so, decanted and precipitated with dilute acetic acid (1 : 8), adding only just sufficient acid to complete the precipitation, and keeping the temperature low. The precipitate is collected on a filter washed with 50 p.c. alcohol, which causes it to shrink and separate easily from the filter; the precipitate is then further washed and extracted with dilute alcohol, strong alcohol, and with ether; then pressed, again washed with alcohol, and dried in a vacuum over oil of vitriol.

If the product is still impure it may be purified by dissolving it in the cold in a very dilute solution of potassium hydroxide (0·1–0·2 p.c.), and, after decanting from any insoluble matter, reprecipitating with dilute acetic acid.

Conglutin was obtained in a similar manner from sweet and bitter almonds and from lupins. It contains rather more nitrogen, is more glutinous, and more soluble in acetic acid than legumin, besides being completely soluble in dilute salt solution. Also, its compound with copper oxide differs a little from the legumin copper-oxide compound.

Gluten-casein was prepared from the seeds of *graminaceæ* in a very similar way.

Ritthausen formed compounds of plant casein with copper oxide by dissolving the finely powdered proteid in water containing 0·2–0·3 p.c. of potassium hydroxide, largely diluting the solution with water, and adding a solution of blue vitriol and as much caustic potash as is necessary to dissolve the precipitate first formed and give the whole solution a violet colour. The clear solution is then neutralised with dilute sulphuric acid, and the precipitate collected and washed with water till it ceases to give a reaction for sulphates.

Legumin thus treated gives a precipitate containing from 13·5 to 15·5 p.c. of CuO, and the protein is unaltered by the treatment.

Conglutin is, to a slight extent, decomposed by the treatment, and yields a compound containing about 11·6 p.c. of CuO.

Gluten-casein is but slightly altered by this treatment; but its copper oxide compound is somewhat soluble in water, and contains about 14 p.c. CuO.

The legumin obtained from several sources by Ritthausen was found by him to be partially soluble in dilute solutions of salt; but there was little or no difference in composition between the soluble and insoluble portions. The composition of legumin and its allies, as given by Ritthausen, varies somewhat according to their source. There is no doubt that the use of alkalis in the extraction of the proteins, and also their subsequent precipitation by an acid, led to alterations in composition and properties in the proteins which has led to confusion and some erroneous results.

To T. B. Osborne, of the Connecticut Agricultural Experiment Station, and his fellow-workers, notably *G. F. Campbell, S. H. Clapp, R. D. Gilbert*, I. F. Harris, *F. W. Heyl*, and C. G. Voorhees, we are indebted for more exact knowledge of the composition and nature of legumin and other vegetable proteins. Osborne's researches began about the year 1891, and will be found, for the most part, recorded in the Journal of the American Chemical Society and the American Journal of Physiology from that date onwards. A summary of the results is given in The Vegetable Proteins, by Thos. B. Osborne, 1909, in which is a valuable bibliography of the subject.

Osborne has shown that legumin and its congeners are true globulins; he obtains legumin (and similar proteins) without the aid of alkalis. The finely ground material, peas or vetches, is extracted with petroleum naphtha to remove oil and treated with a strong solution (10-20 p.c.) of common salt. After filtering the liquid is treated with ammonium sulphate, the resulting precipitate redissolved in 10 p.c. sodium chloride solution, and the liquid dialysed free from chlorides when the protein separates in spheroids. It is washed with water and alcohol and dried over sulphuric acid.

Legumin thus prepared is insoluble in water; when freshly prepared and not dried it is readily soluble in a 10 p.c. solution of sodium chloride. After washing with alcohol and drying it becomes less soluble. A solution in 10 p.c. sodium chloride is not precipitated by saturating the solution with magnesium sulphate or with sodium chloride; nor by sodium sulphate at the ordinary temperature, but is precipitated at 34°. Saturation with ammonium sulphate at common temperatures completely precipitates it. In a salt solution, legumin is precipitated by picric, tannic, hydrochloric, nitric, sulphuric, or acetic acids, but not by mercuric chloride. It is readily soluble in dilute alkalis and alkaline carbonates.

Hammarsten (Zeitsch. physiol. Chem. 1918, 102, 85) regards the legumin of Osborne (*a*-legumin) which is soluble in dilute salt solutions as different from the insoluble legumin of Ritthausen (*b*-legumin) which appears to be an acid meta-protein. *a*-Legumin forms a compound with acid which, however, is not *b*-legumin, because the latter swells in water, giving a viscid non-filterable solution, whereas the acid compound of *a*-legumin does not swell in water, but gives a limpid milky emulsion which filters rapidly, yielding an opalescent filtrate. There are other differences which indicate that *b*-legumin is not formed by the action of acid, alkali or water, but is a distinct protein.

The monoamino-acids from legumin have been studied by Abderhalden and Barkin (Zeitsch. physiol. Chem. 1906, 47, 354).

The protein described under the name of conglutin by Ritthausen, obtained from almond and peach kernels, has been shown by Osborne to be different in some of its characters from legumin, and he has restored to it the name *amandin*, first given to it by Proust in 1802.

The name conglutin Osborne retains for the protein of lupins.

The percentage composition of some of the typical and purest preparations is as follows:—

—	Legumin from peas and beans Ritthausen	Legumin from peas and vetches. Osborne	Conglutin or amandin from almonds Ritthausen	Conglutin or amandin from almonds Osborne	Conglutin from lupins. Ritthausen	Conglutin from lupins. Osborne
C .	51·5	52·1	50·4	51·3	50·8	51·0
H	7·0	7·0	6·9	6·9	6·9	6·9
N .	17·1	18·0	18·1	19·3	18·4	18·0
S .	0·4	0·4	0·4	0·4	0·9	0·4
O .	24·0	22·5	23·7	22·0	23·0	23·7

Globulins have been found in walnuts, hazelnuts, candle-nuts (*Aleurites triloba* [Forst.]), para-nuts (*Bertholletia*), castor-oil beans, cherry kernels, plum and apricot kernels, earth nuts (*Arachis hypogæa* [Linn.]), hemp seed, cotton seed, coconuts, sunflower seeds, and several other seeds.

Ritthausen obtained the following percentages of legumin from different seeds:—French beans 11 p.c., peas 5·4 9·4 p.c., horse beans 10 p.c., Mazagan beans 18·7 p.c., and lentils 5·2 p.c. From sweet almonds he obtained 15 p.c. of conglutin, and from lupins 20 p.c.

The whole of the nitrogenous matter of these seeds is not in the form of legumin; other proteins are present. Thus field beans contain about 23 p.c., and lentils 25 p.c. of nitrogenous matter.

The products of the hydrolysis of legumin with acid and alkalis are those of the proteins generally, the nitrogen being found as ammonia, arginine, and other bases, glycine, alanine, leucine, tyrosine, phenylalanine, aspartic acid, glutamic acid, and other amino acids and tryptophan. Osborne and Harris found, on decomposing with strong hydrochloric acid, that of the total nitrogen 9·3 p.c. was obtained as ammonia, 28·4 p.c. as basic nitrogen, mainly in the forms of arginine, histidine, and lysine, and 61·4 p.c. as non-basic nitrogen.

In China and Japan a kind of vegetable cheese, known in the latter country as *tofu*, is made from the seed of the soy bean (*Glycine hispida* [Maxim.]). This leguminous seed contains about 37-40 p.c. of nitrogenous matter, and about 20 p.c. of fat, being a very concentrated food. Its globulin (glycinin) is very like legumin from peas, but contains rather more sulphur (0·8 p.c.) and rather less nitrogen (17·5 p.c.).

The cheese is made by soaking the beans in water, pounding them, and straining through a sieve, which removes most of the starch, boiling the residue with water, and straining the solution through cotton-cloth and pressing the residue. The strained liquor, containing the nitrogenous matter (legumin, &c.) and fat, is precipitated by the addition of the brine formed on the deliquescence of common sea salt; the precipitate pressed and cut into cakes is ordinary *tofu*. It contains about 89 p.c. of water, the dry matter being nearly two-thirds nitrogenous matter and one-third fat, with small quantities of carbohydrates and ash. A drier product is obtained by freezing these cakes of cheese, and then thawing by exposure to the sun. On thawing, a large quantity of water runs off, leaving a spongy, somewhat horny residue, known as *kori-dofu*.

Analyses of these products gave the following results :—

	Fresh tofu	Frozen tofu or kori-dofu	Dry matter from frozen tofu
Water . .	89·0	18·8	—
Ash . .	0·5	1·6	2·0
Fat . .	3 2	28·8	35·4
Nitrogenous matter	6·5	48 8	60·1
Carbohydrates	0·8	2·0	2·5
	100·0	100·0	100·0

E. K.

LEHRBACHITE *v.* SELENIUM.

LEIPSIC YELLOW. *Normal lead chromate* (*v.* CHROMIUM).

LEITHNER'S BLUE. *Cobalt blue* (*v.* PIGMENTS).

LEMNIAN EARTH, *Terra lemnia*, or *Sphragidite*. A red, yellow, or grey earthy substange, somewhat resembling fuller's-earth, and consisting of a hydrated aluminium silicate, with more or less iron. Dana places it under the clay mineral cimolite ($2Al_2O_3 \cdot 9SiO_2 \cdot 6H_2O$). It takes its name from its occurrence at Lemnos, an island in the Grecian Archipelago, where, in consequence of its reputed medicinal virtues, it was formerly regarded as sacred. The earth was dug only once a year, with much ceremony, and, after mixture with goat's blood, was made into small cakes or balls, which were stamped with a seal by the priests, whence it was termed *terra sigillata*.

Lemnian reddle (*Rubrica lemnia*) was a red ochreous earth used as a colouring material.

L. J. S.

LEMON. The fruit of *Citrus medica* (Linn.) [*C. limonum*]. There are many varieties. König gives as the average of 33 analyses —

Mean weight of a fruit	The fruit consists of Skin	Flesh	Seeds
153 grammes	38·5	59·2	2·3

The fruit contains —

Water	Invert sugar	Citric acid	Nitrogenous matter	Ash
82·6	0·4	5·4	0·7	0 6

The juice contains—

Total extract	Invert sugar	Cane sugar	Citric acid	Nitrogenous matter	Ash
10·44	1·42	0·52	5·83	0·32	0·20

The rind of Italian lemons contains—

Water	Nitrogen	Essential oil	Ash
76·38	0·23	1·01	0·52

The ash of lemons (whole fruit) contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	SiO_2	Cl
43·2	2·7	30·2	5·1	0·6	0·4	13·6	3·1	0 7	0·5

Boric acid, to the extent of 6 milligrammes per litre, has been detected in lemon juice (Hebebrand, 1902). Lemons are largely used, both in the form of fruit and also for the preparation of citric acid (*q.v.*) and essence of lemon (*q.v.*). Lemon juice, both in its raw and concentrated (5 to 7 times) state, is also an important commercial product. According to the British Pharmacopœia lemon juice should have a sp.gr. of 1·030 to 1·040 and 20 millilitres should require for neutralisation not less than 20 and not more than 25·7 millilitres of N/1 solution of sodium hydroxide, corresponding to a proportion of not less than 7 and not more than 9 grammes of citric acid in 100 millilitres. The residue on evaporation dried at 110° should yield not more than 3 p c. of ash.

H. I.

LEMON-GRASS OIL *v. Verbena*, art. OILS, ESSENTIAL.

LEMON, OIL OF, *v.* OILS, ESSENTIAL.

LEMON YELLOW *v.* BARIUM CHROMATE and CHROMIUM.

LENICET. Trade name for basic aluminium acetate.

LENTILS. The seeds of *Lens esculenta* (Moench.) [*Ervum lens*]. These are small in size and are largely used as human food. They are very nutritious, but unless thoroughly cooked are difficult of digestion.

There are many varieties, differing considerably in size and also in composition.

Balland (Compt. rend. 1897, 125, 119) found the following range of variation in composition :—

Weight of 100 seeds grammes	Water	Protein	Fat	N-free extract	Crude fibre	Ash
2·5	11·7	20·3	0·6	56·1	3·0	2·0
to 6 6	13·5	21·2	1·5	62·4	3·6	2·7

Church (Food Grains of India, 1886 and 1891) gives analyses of husked and whole lentils—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Husked .	11·8	25·1	1·3	58·4	1·2	2·2
Unhusked .	11·7	24·9	1·5	56·0	3·6	2·3

König quotes as an analysis of the ash—

Per cent. of ash in dry substance	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	Cl
2·07	34·8	13·5	6·3	2·5	2·0	36 3	4·6

Lentils thrive in temperate climates, and best on a dry calcareous soil ; their leaves and stems, when cut in the early stages of growth, furnish nutritious food for cattle and yield a hay which is excellent for dairy cows.

H. I.

LENTIN. Trade name for *m*-phenylenediamine hydrochloride.

LENTISCUS or **LENTISK.** The leaves of *Pistacia lentiscus* (Linn.), a small shrub growing wild in Tunis. Contain from 10 to 12 p.c. of tannin and are used in admixture with sumach, the dried leaves of *Rhus coriaria* (Linn.), in tanning. For methods of detecting and estimating lentiscus in sumach, *v.* Scarlata (J. Soc. Chem. Ind. 1900, 779).

LEONITE, Kaliblœdite, or Kaliastrakanite. A double salt $K_2SO_4 \cdot MgSO_4,4H_2O$, crystallised in the monoclinic system and corresponding with blœdite ($Na_2SO_4 \cdot MgSO_4,4H_2O$). It occurs usually in the massive form, but occasionally as tabular crystals, associated with kainite in the

Prussian salt deposits at Wilhelmshall, Westeregeln, and Leopoldshall. The artificial salt, known as kaliastrakanite, was known previously to the discovery of the natural mineral in 1896.

L. J. S.

LEPIDINE *v.* QUINOLINE

LEPIDOLITE *v.* LITHIUM, also MICA.

LEPTANDRA. *Culver's Root.* The rhizome and rootlets of *Veronica* (*Leptandra*) *virginica* (Linn.) contain a resin leptandrin. It is used as a cathartic in biliousness or constipation.

LEPTOCHLORITE *v.* THURINGITE.

LEPTOSPERMOL. A phenolic substance found in the essential oil obtained from the leaves and terminal branches of *Leptospermum flavescens.* A colourless viscous liquid, of a pleasant odour, giving with ferric chloride in alcoholic solution a brilliant orange-red coloration and an intense blue with copper salts. B.p. 146°/10 mm; 275°–278°/770 mm. D20 = 1·073, $n_D^{28°}$ 1·50. Possibly identical with tasmanol found in certain eucalyptus oils (Penfold, Perf. Ess. Oil. Rec. 1921, 12, 336).

LEPTYNOL. Trade name for colloidal palladous hydroxide in sesamé oil.

LETHAL *see Spermaceti*, art. WAXES.

LETTUCE. *Lactuca scariola* (Linn.) and other species. Several varieties are known. The leaves are eaten as a salad

Konig gives as the average composition of the usual species

Water	Nitrogenous substances	Fat	N-free extract	Crude fibre	Ash	Organic sulphur
94·3	1·4	0·3	2·2	0·7	1·0	0·01

The ash contains

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
37·6	7·5	14·7	6·2	5·3	9·2	3·8	8·1	7·6

The juice contains potassium hydrogen citrate.

All lettuces possess slight narcotic properties, and the milky juice of certain species, especially *L. virosa* (Linn.), when evaporated, yields a brown, viscid residue which has been used in medicine under the name "lactucarium" (*q.v.*).

H. I.

LETTUCE OPIUM *v.* LACTUCARIUM

LEUCACENE (*peri*-diacenaphthylene-rhodacene), a hydrocarbon formed when acenaphthene is distilled through a red-hot tube Forms colourless platelets or silky needles, m.p. 250°; crystallises from benzene as $4C_{54}H_{12}.5C_6H_6$. When heated at 175° under reduced pressure it decomposes into acenaphthylene and rhodacene. Becomes pink on exposure to air, and yields naphthoic acid on oxidation with chromic acid (Dziewonski, Ber. 1920, 53 [B], 2173).

LEUCANILINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

LEUCINE. The name *leucine*, suitably prefixed, is given to the four following monoaminocaproic acids:—

1. *l-Leucine* (*α-amino-γ-methylvaleric acid*)

$$(CH_3)_2CH·CH_2·CH(NH_2)CO_2H.$$

2. *d-iso-Leucine* (*α-amino-β-methylvaleric acid*)

$$CH_3·CH_2·CH(CH_3)CH(NH_2)CO_2H.$$

3. *n-Leucine* (*α-amino-n-hexoic acid*)

$$CH_3[CH_2]_3CH(NH_2)CO_2H.$$

4. *ε-Leucine* (*ε-amino-n-hexoic acid*)

$$H_2N·CH_2[CH_2]_4CO_2H.$$

With the exception of the last they all occur among the degradation products of a great many of the proteins.

l-**Leucine**, *α-amino-γ-methylvaleric acid*

$$(CH_3)_2CH·CH_2·CH(NH_2)CO_2H$$

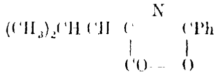
is, next to arginine, the most widespread of the amino acids that occur in proteins. It was discovered by Proust (Ann. Chim. 1818, [ii.] 10, 40) in decaying cheese and called "oxide-caséux"; Braconnot (*ibid.* 1820 [ii.], 13, 19) isolated it from the products of the acid hydrolysis of meat, and named it leucine (λευχός) because of the glistening white crystals it forms. Mulder (J. pr. Chem. 1839, 16, 290) established the identity of the two substances and also obtained it by boiling meat with alkali and by the putrefaction of casein.

Leucine occurs in the free state in many of the organs of the animal body, in the tissues of the lung (Cloetta, Annalen, 1851, 92, 289), in the thymoid and thyroid glands and the pancreas (Gorup-Besanez, Annalen, 1856, 98, 7; Radziewsky, Zeitsch. Chem. 1866, 416), in the brain (Muller, Annalen, 1857, 103, 131); it is found in the liver and urine under certain pathological conditions (Frerich and Stadeler, J. 1854, 678; 1856, 702; 1858, 550; Salkowsky, J. Thierchem. 1880, 457; Valentiner, J. 1854, 675; Sotnitschwski, Zeitsch. physiol Chem. 1879, 3 391); in the blood (Abderhalden, Zeitsch. physiol. Chem. 1913, 88, 178; Lippich, *ibid.* 1911, 90, 124). Leucine occurs in the pupæ of butterflies (Schwarzenbach, J. 1857, 538), in spiders and in crayfish, and also in the typhus bacillus, Tamura (Zeitsch. physiol Chem. 1914, 89, 289). In the vegetable kingdom leucine has been found in the juice of etiolated vetch seedlings (Gorup-Besanez, Ber. 1874, 7, 146; Cossa, Gazz. chim. ital. 1876, 6, 314), also in the young green plants (Schulze, Landw. Versuchs. Stat 1895, 46, 383); in potatoes (Schulze and Barbieri, *ibid.* 24, 167); in young pumpkin plants (Schulze and Barbieri, Ber. 1878, 11, 1233); in fungi (Winterstein, Zeitsch physiol. Chem. 1899, 26, 438); in the pod of the broad bean (Bourquelot and Hérissey, J. Pharm. Chim. 1898, [vi.] 8, 385); and in beet juice (Ehrlich, Zeit. Ver. deut. Zuckerind. 1903, 571, 809).

l-Leucine crystallises in glistening white leaves, melts at 280° when rapidly heated (Trans. Guinness Res. Lab. 1903, i. 57), and has sp.gr. 1·293, in absolute alcohol at 18° (Engel and Vilmain, Bull. Soc. chim. 1874, [ii.] 22, 279). It dissolves in 46 parts of water at 18° (Schulze, Zeitsch. physiol. Chem. 1884, 9, 254); in 1040 parts of cold alcohol (96 p.c.) or in 800 parts of hot alcohol (98 p.c.) (Zollikoffer, Annalen, 1852, 82, 176); in 10·9 parts of glacial acetic acid at 15° or 29·32 parts at 117° (Habermann and Ehrenfeld, Zeitsch. physiol. Chem. 1902, 37, 18). The molecular heat of combustion is 854·9 Cal., and the heat of formation 158·4 Cal. (Berthelot and André, Compt. rend. 1890, 110, 884). Natural leucine or *l*-leucine is lævorotatory in aqueous and dextrorotatory in acid or alkali solution (Lewkowitsch, Ber. 1884, 17, 1439), and has $[\alpha]_D + 15·6°$ in hydrochloric acid solution (Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 399); it remains unchanged on boiling with concentrated hydrochloric acid (Abderhalden and Wurm (Zeitsch. physiol. Chem 1912, 32, 167); when heated with barium hydroxide solution at 150°–160° for three days it is racemised, and the inactive leucine can be resolved by the action of *Penicillium glaucum*, yielding *l*-leucine, the rotation of which is equal in magnitude and opposite in direction to that of the lævo isomeride (Schulze and Bosshard, Zeitsch. physiol. Chem. 1886, 10, 140). *See* Schneider and Hurler (Chem. Zentr 1914, 1, 401) for its germicidal effects, especially against the typhus bacillus.

The constitution of leucine as α-amino-γ-methylvaleric acid was first established by Schulze and Likiernik (Ber. 1891, 24, 669), who showed that the synthetic α-amino*iso*butylacetic acid (α-amino-γ-methylvaleric acid) prepared by Hufner (J. pr. Chem 1870, [ii.] 1, 6) by the action of ammonia and hydrogen cyanide on *iso*valeraldehyde, was identical with the inactive leucine obtained by heating natural *l* leucine with barium hydroxide. The two compounds have the same solubility in water, 1 part in 105 at 13°; yield the same *d* leucine when used as a culture medium for *Penicillium glaucum*, and give the same leucic acid (hydroxycaproic acid), m.p. 54·5° on treatment with nitrous acid.

Further syntheses of *r*-leucine are described by (1) Erlenmeyer and Kunlin (Annalen, 1901, 316, 145), who obtained the anhydride



$$
\begin{array}{l}
\qquad\qquad\qquad\qquad\quad \mathrm{N} \\
(\mathrm{CH_3})_2\mathrm{CH{\cdot}CH{:}C} \qquad \mathrm{CPh} \\
\qquad\qquad\qquad\quad\;\; | \qquad\quad | \\
\qquad\qquad\qquad\quad \mathrm{CO}{-}{-}\mathrm{O}
\end{array}
$$

of α-benzoylamino-β-*iso*propylacrylic acid by condensing hippuric acid and *iso*butyraldehyde in the presence of acetic anhydride: the corresponding acid $(CH_3)_2CH{\cdot}CH{:}C(NH{\cdot}COPh)CO_2H$ when heated with excess of ammonia solution at 150°–170° is hydrolysed, yielding *r*-leucine, *iso*valeric, and benzoic acids. (2) Bouveault and Locquin (Bull Soc. chim. 1904, [iii.] 31, 1180) from ethyl α-oximino*iso*hexoate

$$(CH_3)_2CH{\cdot}CH_2{\cdot}C(NOH)CO_2Et$$

obtained by the action of nitrosyl sulphate on ethyl *iso*butylacetoacetate; this on reduction yielded ethyl α-amino*iso*hexoate

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2)CO_2Et$$

from which by hydrolysis *r*-leucine was obtained. (3) Fischer and Schmitz (Ber. 1906, 39, 351) who obtained *r*-leucine from ethyl *iso*butylmalonate $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ by converting into the bromo derivative

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CBr(CO_2Et)_2$$

hydrolysing this ester, and converting the *iso*butylbromomalonic acid thus obtained into *iso*butylbromoacetic acid

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H$$

by distillation under reduced pressure; this on treatment with ammonia yielded *r*-leucine $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$.

r-Leucine has been resolved into *d*- and *l*-leucine by the fractional crystallisation of certain alkaloid salts of the benzoyl and formyl derivatives (*q.v.*) (Fischer, Ber. 1900, 33, 2370; Fischer and Warburg, *ibid.* 1905, 38, 3997).

Derivatives. *Salts.—Mercury salt*

$$(C_6H_{12}O_2N)_2Hg$$

formed by dissolving mercuric oxide in a solution of leucine (Gössmann, Annalen, 1854, 91, 134); *lead salt* $(C_6H_{12}O_2N)_2Pb,H_2O$ crystallises in leaves (Strecker, Annalen, 1849, 72, 90); *copper salt* $(C_6H_{12}O_2N)_2Cu$, small light blue crystals, soluble in 3045 parts of cold or 1460 parts of boiling water (Hofmeister, Annalen, 1877, 189, 16). The salts with acids are readily soluble: the two *hydrochlorides* $C_6H_{12}O_2N,HCl$ and $(C_6H_{12}O_2N)_2,HCl$ are described (Laurent and Gerhardt, Ann. Chim. Phys. [iii.] 34, 321; Schwanert, Annalen, 1857, 102, 222); the *nitrate* $C_6H_{12}O_2N,HNO_3$ (Laurent and Gerhardt); the *platinichloride* $(C_6H_{12}O_2N)_2,H_2PtCl_6$ forms a yellow crystalline precipitate; dl-*leucine picrolonate* $C_{10}H_8O_5N_4{\cdot}C_6H_{13}O_2N$ crystallises in long, narrow, greenish-yellow prisms which become yellow when dry; they soften at 130° and melt at about 150° (decomp.), Abderhalden and Weil (Zeitsch. physiol. Chem. 1912, 78, 150. Levene and van Slyke, J. Biol. Chem. 1912, 12, 127, obtained rosettes of six-sided crystals); natural leucine picrolonate crystallises into a mixture of long, slender and rhomboid crystals, Levene and van Slyke (*l.c.*).

Anhydride $(C_6H_{12}ON)_2O$, m.p. 272°, obtained together with its *dibenzoyl* derivative

$$(C_6H_{11}ON{\cdot}C_7H_5O)_2O$$

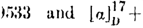
m.p. 80°, by the action of benzoyl chloride on leucine at 100° (Destrem, Compt. rend. 1878, 86, 484; *cf.* Graves, Marshall and Eckweiler, J. Amer Chem. Soc. 1917, 39, 112). *The potassium salt of trimethylleucine iodide*

$$C_5H_{10}(NMe_3I)CO_2K$$

hygroscopic slender needles obtained by the action of methyl iodide and potassium hydroxide on leucine; the corresponding *chloro* compound forms a yellow *aurichloride*

$$C_6H_{11}O_2NMe_3Cl{\cdot}AuCl_3$$

m.p. 163°, and an orange-yellow *platinichloride* $(C_6H_{11}O_2NMe_3Cl)_2PtCl_4$ (Koener and Menozzi Gazz. chim. ital. 1883, 13, 351).

Leucinimide (3:6-di*iso*butyl-2:5-diketopiperazine)  $\mathrm{NH}\!\begin{array}{l}\diagup \mathrm{CH(C_4H_9)CO} \diagdown\\ \diagdown \mathrm{CO{\cdot}(C_4H_9)HC} \diagup\end{array}\!\mathrm{NH}$, m.p. 271° (corr.), yields *leucyl-leucine*

$$NH_2{\cdot}CH(C_4H_9)CO{\cdot}NH{\cdot}CH(C_4H_9)CO_2H$$

on hydrolysis, this crystallises with $1\frac{1}{2}H_2O$, and melts slightly above 270° (Cohn, Zeitsch. physiol. Chem. 1900, 29, 283; Fischer, Ber. 1900, 33, 2370; 1902, 35, 1095; Salaskin, Zeitsch. physiol. Chem. 1901, 32, 592). *l-Leucine methyl ester* has b.p. 79°–79°·5/12 mm., D^{17} 0·9533 and $[\alpha]_D^{17} + 16{\cdot}53°$ (Abderhalden and Spinner, Zeitsch. physiol. Chem. 1919, 107, 1) *Ethyl ester* of *r-leucine* has b.p. 83·5°/12 mm., sp.gr. 0·929 at 17°; the *picrate* has m.p. 136° (corr.), and the *d-tartrate*, m.p. 145° (corr.); the *ethyl ester* of *l-leucine* has $[\alpha]_D^{20°} + 13{\cdot}1°$, and is not racemised on hydrolysis; it forms a *picrate*, m.p. 129·5° (corr.) (Fischer, Ber. 1901, 34, 433; *cf.* Röhmann, *ibid.* 1897, 30, 1978). When the ethyl ester of *r*-leucine is left in contact with water and crude pancreatin, it undergoes asymmetric hydrolysis, that is, the *l*-ester is hydrolysed, whilst the *d*-ester is not (Warburg, Ber. 1905, 38, 187). *n-Propyl ester* of *leucine* has b.p. 95°–96°/12 mm. (Warburg, Zeitsch. physiol. Chem. 1906, 48, 205).

r-Leucinamide $C_6H_{14}ON_2$, m.p. 106°–107° (corr.), is prepared by the action of liquid ammonia on the ethyl ester; the *β-naphthalene sulphonyl derivative* has m.p. 176°–178° (corr.); and *carbethoxy-dl-leucinamide* $C_9H_{18}O_3N_2$, m.p. 108°, readily yields *β-iso*butylhydantoin by shaking with sodium hydroxide (Koenigs and Mylo, Ber. 1908, 41, 4427).

The *ethyl ester* of *l-leucinecarbimide*

$$CO : N{\cdot}CH(CO_2Et)CH_2{\cdot}CHMe_2$$

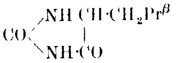
b.p. 120°–130°/18 mm. is formed together with *diethyl leucinecarbimide*

$$CO[NH{\cdot}CH(CO_2Et)CH_2{\cdot}CHMe_2]$$

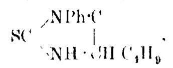
b.p. 180°–190°/18 mm. by the action of carbonyl chloride on the ethyl ester of leucine; *isobutylhydantoic acid*

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_2Pr^{\beta})CO_2H$$

m.p. 200°–210° (with decomposition) is obtained by dissolving leucine in excess of carbamide at 130°–135°, and yields *isobutylhydantoin*



$$CO\begin{array}{l}\diagup NH{\cdot}CH{\cdot}CH_2Pr^{\beta}\\ \qquad\qquad |\\ \diagdown NH{\cdot}CO\end{array}$$

m.p. 200°–210°, when heated at 150°; the *ethyl ester* of *isobutylhydantoic acid* is obtained by the action of ammonia on the ethyl ester of *l*-leucinecarbimide, and this on hydrolysis yields the free acid identical with the substance obtained by the action of carbamide on leucine; when aniline is substituted for ammonia the *acid* $NHPh{\cdot}CO{\cdot}NH{\cdot}CH(CH_2Pr^{\beta})CO_2H$ is obtained, m.p. 115° (Hugounenq and Morel, Compt. rend. 1905, 140, 150, 505, 859). *Leucine phenylthiohydantoin*  $SC\begin{array}{l}\diagup NPh{\cdot}CO\\ \qquad\quad |\\ \diagdown NH{\cdot}CH{\cdot}C_4H_9\end{array}$, m.p. 178°, is formed by the interaction of leucine and phenyl mustard oil in the presence of potassium hydroxide, and its formation affords a convenient method of isolating leucine from the crude material obtained by hydrolysing proteids (Röhman, Ber. 1898, 31, 2188).

Phthalylaminocaproic acid $C_{14}H_{15}O_4N$, prepared by fusing a mixture of phthalic anhydride and leucine, has m.p. 115°–116°; it is lævorotatory, and is converted into the racemic isomeride on dry distillation; the *platodiammonium salt* $Pt(NH_3{\cdot}NH_3C_{14}H_{15}ON)_2$ of the active acid contains $3H_2O$, that of the inactive acid $3\frac{1}{2}H_2O$.

Leucinephthaloic acid

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H)CH_2{\cdot}CHMe_2$$

is obtained by the partial hydrolysis of the preceding compound, the active acid melts and decomposes at 130°–137°, forming phthalylaminocaproic acid; the *potassium salt*

$$K_2C_{14}H_{15}O_5N$$

is crystalline and readily soluble; the *sodium salt* is amorphous; the *barium salt* is crystalline and sparingly soluble; the *platodiammonium salt* forms soluble rhombic plates; the amorphous *copper salt* is soluble in alcohol; the inactive *leucinephthaloic acid* has m.p. 152°–153°, and forms a crystalline *potassium* and an amorphous *silver salt* (Reese, Annalen, 1887, 242, 1; Ber. 1888, 21, 277). The *benzene sulphonic* derivative

$$SO_2Ph{\cdot}HN{\cdot}C_5H_{10}{\cdot}CO_2H$$

of *r*-leucine sinters at 140°, melts at 146° (corr.), and forms soluble crystalline alkali salts, and sparingly soluble lead and silver salts; the corresponding derivative of *d*-leucine crystallises in needles, m.p. 119°–120° (corr.), and has $[\alpha]_D^{20} -39°$ (Fischer, Ber. 1900, 33, 2370; 1901, 34, 449).

Benzoyl-r-leucine

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH{\cdot}COPh)CO_2H$$

m.p. 137°–141° (corr.), can be resolved by means of its alkaloid salts, the cinchonine salt of the *d*- and the quinidine salt of the *l*-isomeride being sparingly soluble. *Benzoyl-d-leucine* melts at 105°–107° (corr.), dissolves in 120 parts of boiling water and has $[\alpha]_D^{20} -6{\cdot}39°$ in sodium hydroxide solution. *Benzoyl-l-leucine* melts at 105°–107° (corr.), has $[\alpha]_D^{20} +6{\cdot}59°$ (Fischer, Ber. 1900, 33, 2370).

Formyl-r-leucine

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(NH{\cdot}CHO)CO_2H$$

forms octahedra, m.p. 115°–116° (corr.); *see* Galeotti (Biochem. Zeitsch. 1913, 53, 485) for the condensation of *r*-leucine with formaldehyde; *formyl leucylchloride*

$$C_4H_9{\cdot}CH(NH{\cdot}CHO)COCl$$

is a crystalline powder. The *brucine* salt of formyl-*d*-leucine is sparingly soluble, and yields on decomposition *formyl-d-leucine*, crystallising in long thin prisms, m.p. 141°–144° (corr.), $[\alpha]_D^{20} +18{\cdot}8°$ in 10 p.c. alcoholic solution. *Formyl-l-leucine* obtained from the more soluble leucine salt has the same melting-point as the *d*- compound and $[\alpha]_D^{20} -18{\cdot}5°$. p-*Toluenesulphonyl-l-leucine*, m.p. 121°, $[\alpha]_D^{20}$ +[illegible]·50° in alcoholic solution, yields p-*toluene-sulphonyl-l-N-methyl-leucine* $CHMe_2{\cdot}CH_2{\cdot}CH(NMe{\cdot}SO_2C_7H_7)COOH$, m.p. 91–92°, $[\alpha]_D^{18} -21{\cdot}12°$, and this on hydrolysis gives *l-N-methyl-leucine*, $[\alpha]_D^{21} +29{\cdot}76°$ in aqueous solution, it sublimes in needles when carefully heated and yields a crystalline nitrate and hydrochloride and the copper salt

$$C_{14}H_{28}O_4N_2Cu,H_2O$$

forms four or six-sided plates. Fischer and Lipschitz (Ber. 1915, 48, 360). Leucine heated with diphenylmethane at 170°–180° yields cycloleucylleucine, Graziani (Atti. R. Accad. Lincei, 1915 [5], 24, 1, 822); Maillard, Ann. Chim. 1915 [9], 3, 48). For a description of the numerous *polypeptides* containing the leucyl radicle, *see* Fischer and Bargell, Ber. 1903, 36, 2592; Fischer and Brunner, Annalen, 1905, 340, 142; Fischer and Warburg, *ibid.* 152; Fischer and Koelker, *ibid.* 172; Fischer, Ber. 1905, 38, 2914; 1906, 39, 2893; Fischer and Steingroever, Annalen, 1909, 365, 167; Fischer and Gerngross, Ber. 1909, 42, 1485; Fischer and Gluud, Annalen, 1909, 369, 247; Fischer and Fielder, *ibid.* 1910, 375, 181; Abderhalden and Hirszowski, Ber. 1908, 41, 2840; Abderhalden, *ibid.* 1909, 42, 2331; Abderhalden, Hirsch, and Schuler, *ibid.* 1909, 42, 3394; 1910, 43, 907; Abderhalden and Weber, *ibid.* 1910, 43, 2429; Hans Fischer, *ibid.* 1909, 42, 4320; Krause, Monatsh. 1908, 29, 1119; Hopwood and Weizmann, Chem. Soc. Trans. 1911, 99, 574, 1579; Abderhalden and Fodor, *ibid.* 1916, 49, 561; Zeitsch. physiol. Chem. 1912, 81, 1; Ber. 1916, 49, 561; Weizmann and Hopwood, Proc. Roy. Soc. 1913, A, 88, 455.

For the preparation and properties of the corresponding amino-alcohol and choline from leucine, *see* Karrer, Karrer, Thomann, Horlacher and Mader (Helv. Chim. Acta, 1921, 4, 76).

Decomposition.—Experiments conducted on dogs show that leucine, like other amino acids, can replace ammonium salts in the formation of urea (Salaskin, Zeitsch. physiol. Chem. 1898, 25, 128). Leucine as well as tyrosine is assimilated by certain plants such as *Algæ* (Loew and Bokorny, J. pr. Chem. 1885, [ii.] 36, 279; Schulze, Landw. Versuchs. Stat. 1901, 56, 97), *Cucumis* species *Aspergillus niger*, *A. repens*, *Penicillium glaucum* (Lutz, Compt. rend. 1905, 140, 380; Petrov, Bull. Agr. Intelligence, 1914, 5, 210). Yeast poor in nitrogen develops rapidly in a sugar solution containing leucine; when racemic leucine is employed the fermentation proceeds at the expense of both optical isomerides, but the natural *l*-leucine is destroyed much more rapidly than the *d* leucine, which can thus be recovered to the extent of 76 p.c. of the theoretical quantity at the end of the reaction (Ehrlich, Zeit. Ver. deut. Zuckerind. 1906, 608, 840). The degradation of amino acids in the plant and animal economy appears to be deamidisation and oxidation of the terminal carbon atom (Sachs, Biochem. Zeitsch. 1910, 27, 27), this would lead in the case of leucine to the formation of ammonia and amyl alcohol; and Ehrlich (Ber. 1906, 40, 1027) is of opinion that the occurrence of fusel oil during alcoholic fermentation is due to the hydrolysis of *l*-leucine and *d*-*iso*leucine according to the equations:

$$\mathrm{CHMe_2{\cdot}CH_2{\cdot}CH(NH_2)CO_2H + H_2O}$$
$$\mathrm{= CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH + CO_2 + NH_3}$$
$$\mathrm{CHMeEt{\cdot}CH(NH_2)CO_2H + H_2O}$$
$$\mathrm{= CHMeEt{\cdot}CH_2{\cdot}OH + CO_2 + NH_3}$$

On oxidation with hydrogen peroxide leucine yields *iso*valeraldehyde, *iso*valeric acid, ammonia and carbon dioxide; on further oxidation acetone is formed from *iso*valeric acid, the reaction closely resembling several biochemical reactions in which leucine takes part (Dakin, J. Biol. Chem. 1908, 4, 63).

By the action of nitrous acid leucine is converted into leucic acid (α-hydroxy*iso*hexoic acid) (Strecker, Annalen, 1848, 68, 55); and on reduction with hydriodic acid yields caproic acid and ammonia (Hufner, Zeitsch. Chem. 1868, 391). *l*-Leucic acid sinters at 78° and melts at 81°–82°, $[\alpha]_D^{20} - 27{\cdot}8°$ in alkaline solution; *d*-leucic acid melts at 80° and has $[\alpha]_D + 26{\cdot}3°$ in alkaline solution (Scheibler and Wheeler, Ber. 1911, 44, 2684).

Separation and detection.—A mixture of leucine and tyrosine is readily separated by the aid of boiling glacial acetic acid in which the leucine is fairly (29·23 at 117°) and the tyrosine very sparingly soluble (0·18 at 117° (Habermann and Ehrenfeld, Zeitsch. physiol. Chem. 1902, 37, 18). To separate tyrosine, leucine, and valine, Levene and Jacobs (Biochem. Zeitsch. 1908, 9, 231) recommend the following method. The mixture is treated with bromine, and the bromo derivative of the tyrosine removed by means of amyl alcohol; the valine and leucine are crystallised from the mother liquor, redissolved, and the leucine precipitated by lead acetate and ammonia. On decomposing the lead precipitate with sulphuretted hydrogen, leucine and *iso*leucine are obtained and can be separated by extracting the copper salts with methyl alcohol in which the copper derivative of *iso*leucine is soluble. Glutamic acid and leucine can be separated by saturating the solution with hydrogen chloride when the insoluble hydrochloride of glutamic acid is precipitated (Etard, Compt. rend. 1901, 133, 1231).

Leucine heated with dilute sulphuric acid and potassium bichromate gives a characteristic smell not given by other monoamino acids (Morner, Zeitsch. physiol. Chem. 1913, 88, 152).

Like other α-amino carboxylic acids leucine gives a blue colour if carefully treated with triketohydrindenehydrate in alkaline solution (Abderhalden and Schmidt, *ibid.* 1911, 72, 37–43, and *ibid.* 1913, 85, 146).

In order to test for small traces of leucine the uramino reaction may be used and typical crystals of *iso*butyl hydantoic acid obtained (Lippich, Zeitsch. physiol. Chem. 1911, 90, 148; *see* also Ber. 1906, 39, 2953).

d-*iso***Leucine**, *α-amino-β-methylvaleric acid* $\mathrm{CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(NH_2)CO_2H}$ was discovered by Ehrlich (Zeit. Ver. deut. Zuckerind. 1903, 571, 809; Ber. 1904, 37, 1809) in the mother liquor of the beet sugar manufacture to which the strontia desaccharification process had been applied; it is separated from the *r*- and *l*-leucine that occur with it by the aid of its copper salt which dissolves freely in methyl alcohol, the corresponding salt of leucine being only sparingly soluble. *iso*Leucine has also been isolated from the products of hydrolysis obtained by digesting blood fibrin with pancreatic juice, from the hydrolytic products of ovalbumin, from the crude leucine obtained by the putrefaction of beef (Ehrlich, *l.c.*); and from the products of hydrolysis of casein (Weitzenböck, Monatsh. 1906, 27, 831). It is probable indeed that *d*-*iso*leucine occurs invariably along with *l*-leucine as a primary product of proteid hydrolysis (Ehrlich, *l.c.*; Ehrlich and Wendell, Biochem. Zeitsch. 1908, 8, 399).

d-*iso*Leucine crystallises in shining rods or leaflets, which melt and decompose at 280° when heated in a closed tube; it has $[\alpha]_D^{20} + 9{\cdot}74°$ in aqueous, $+36{\cdot}80°$ in 20 p.c. hydrochloric acid, or $+11{\cdot}1°$ in alkaline solution, and dissolves in 25·84 parts of water at 15·5°, the solution having a bitter taste. It is completely racemised and partially converted into *alloisoleucine* after heating for 20 hours at 180° with barium hydroxide solution (Ehrlich, Ber. 1904, 37, 1809).

Locquin (Bull. Soc. chim. 1907, [iv.] 1, 595, 601) finds slightly different physical constants for the synthetic *d*- and *l*-*iso*leucine; both compounds crystallise from water in brilliant spangles, and have m.p. 280°–290°; *l*-*iso*leucine has $[\alpha]_D^{20} - 10{\cdot}55°$ in aqueous, $-31{\cdot}37°$ in dilute or $-40{\cdot}86°$ in concentrated hydrochloric acid solution, and *d*-*iso*leucine has $[\alpha]_D^{20} + 11{\cdot}29°$ in aqueous or $+40{\cdot}61°$ in concentrated hydrochloric acid solution.

When *d*-*iso*leucine is subjected to dry distillation it yields partially racemised *d*-amylamine $CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}NH_2$, together with *iso*-leucinimide; and it is decomposed by yeast growing in a sugar solution to form *d*-amylalcohol

$$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(NH_2)CO_2H+H_2O$$
$$=CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}OH+NH_3+CO_2$$

It follows, therefore, that *iso*leucine is α-amino, β-methylvaleric acid, and this view of its constitution is confirmed by various synthetic preparations. (1) Bouveault and Locquin (Compt. rend. 1905, 141, 115) prepared an inactive leucine from ethyl *sec*butylacetoacetate

$$CHMeEt{\cdot}CHAc{\cdot}CO_2Et$$

this yields ethyl α-oximino-*sec*butylacetate (α-oximino-β-methylvalerate)

$$CHMeEt{\cdot}C(NOH){\cdot}CO_2Et$$

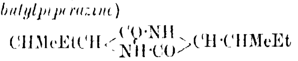
by the action of nitrosylsulphate, which on reduction is converted into the inactive leucine $CHMeEt{\cdot}CH(NH_2)CO_2H$. On resolving this compound by the fractional crystallisation of the brucine salt of its formyl derivative, *d-iso*-leucine was obtained, identical with Ehrlich's natural product (Locquin, Bull. Soc. chim. 1907, [iv.] 1, 595, 601). (2) Ehrlich (Ber. 1907, 40, 2538) synthesised *iso*leucine from *d* amyl-alcohol $CHMeEt{\cdot}CH_2{\cdot}OH$, by the following series of reactions, the *d*-amyl alcohol was oxidised to *d*-valeraldehyde $CHMeEt{\cdot}CHO$, which was converted by the action of ammonia and hydrogen cyanide into aminovaleronitrile $CHMeEt{\cdot}CH(NH_2)CN$, and thus, on hydrolysis, gave a mixture of *d-iso*leucine and *alloisoleucine* $CHMeEt{\cdot}CH(NH_2)CO_2H$. Allo*iso*leucine is a stereoisomide of *isol*eucine, which contains two asymmetric carbon atoms; it closely resembles *iso*leucine in its external appearance, and in the properties of its derivatives; it has, however, a sweet taste, is lævorotatory, $[\alpha]_D^{20}$ −14·4° in aqueous and 26·95° in hydrochloric acid solution; and it dissolves in 31·2 parts of water at 20°. (3) Using Fischer's method (Ber. 1906, 39, 351), Ehrlich (*ibid.* 1908, 41, 1453) has synthesised racemic *iso*leucine from secondary butyl iodide and ethyl malonate, on hydrolysing the condensation product of these two compounds, Romburgh's *sec*butylmalonic acid is obtained; this on bromination yields bromo-*sec*butyl-malonic acid $CHMeEt{\cdot}CBr(CO_2H)_2$, which decomposes when distilled under reduced pressure yielding α-bromo-β-methylvaleric acid

$$CHMeEt{\cdot}CHBr{\cdot}CO_2H$$

on treating this compound with ammonium hydroxide it is converted into racemic *iso*leucine, m.p. 275° in a closed tube. The same synthesis was made by Brasch and Friedmann (Beitr. Chem. Physiol. Path. 1908, 11, 376).

Derivatives. *Salts.*—*d*-iso*Leucine-hydrochloride* forms stellate needles; the *copper salt* $C_{12}H_{22}O_4N_2Cu$ is deep blue and crystalline, dissolves in 278 parts of water at 17°, in 476 parts of 99 p.c. alcohol, and in 55 parts of methyl alcohol at 17°; the *silver salt* is white flocculent and crystalline; the *lead salt* is strongly lævorotatory; *d*-iso-*leucine picrolonate*, forms long, slender, six-sided crystals grouped in stars, m.p. about 170°, $[\alpha]_D^{20}$ +32·8° (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127).

Acyl derivatives of (1) *r-iso*leucine, the *formyl* derivative has m.p. 121°–122°; the *benzoyl* derivative has m.p. 79°, and b.p. 211°/15 mm.; the *benzenesulphonyl* derivative has m.p. 169°; and the *p-toluenesulphonyl* derivative has m.p. 139°. (2) *d-iso*Leucine, *formyl* derivative forms fine translucent crystals from water, m.p. 156°–157°, $[\alpha]_D^{20}$ +28·26°; *benzoyl* derivative, m.p. 116°–117°, $[\alpha]_D^{20}$ +26·36° in alkaline solution; *benzenesulphonyl* derivative, m.p. 149°–150°, $[\alpha]_D^{20}$ 12·04° in alkaline solution; the *phenylisocyanate*, m.p. 119°–120°, $[\alpha]_D^{20}$ +14·92° in alkaline solution; the *phenylhydantoin* has m.p. 78°–79°; *leucinimide* (*iso-2 : 5-diketo-3 : 6-diisobutylpiperazine*)



$$CHMeEtCH{<}{\substack{CO{\cdot}NH\\NH{\cdot}CO}}{>}CH{\cdot}CHMeEt$$

forms slender needles, m.p. 280°–281°, and is slightly dextrorotatory in alcoholic solution. (3) *l-iso*Leucine, *formyl* derivative has m.p. 156°–157°, and has $[\alpha]_D^{20}$ −27·76° in alcoholic solution; the *benzoyl* derivative has m.p. 118° and $[\alpha]_D^{20}$ −26·03° in *N*/2 sodium hydroxide. For the description of *polypeptides* containing the *iso*leucine radicle, *see* Abderhalden, Hirsch, and Schuler, Ber. 1909, 42, 3394; 1910, 43, 907.

n-**Leucine**, *α-amino-n-hexoic acid*

$$CH_3[CH_2]_3CH(NH_2)CO_2H$$

has not been isolated from the products of hydrolysis of proteins, but *n*-valeric acid is formed when casein is oxidised by bromine (Skraup and Witt, Monatsh. 1906, 27, 663), and this suggests the presence of *n*-leucine in casein. Further evidence in favour of this suggestion was obtained by Heckel (Monatsh. 1908, 29, 15), who found that by oxidising with potassium permanganate that fraction of the leucine esters from casein least soluble in hydrochloric acid, a mixture of acids was obtained about one half of which was *n*-valeric acid. Samec (Monatsh. 1908, 29, 55) also obtained a similar result, using the leucine obtained from the neck band of the ox. Kudelka (Monatsh. 1908, 29, 351) has prepared *n*-leucine by Fischer's method (Ber. 1900, 33, 2320) from both natural and synthetic *n*-hexoic acid, using Kahlbaum's preparation; 100 parts of the former gave 37 parts of *n*-leucine, whilst 100 parts of the latter gave only 6 parts. Racemic *n*-leucine melts at 290° (corr.) in a closed tube. The *copper* salt forms pale blue leaflets, the *nickel* salt is greenish-blue, the *cobalt* salt crystallises in red leaflets; the methylated base yields a yellow *aurichloride* $C_9H_{19}O_2N,HAuCl_4$, m.p. 142°.

The resolution of racemic *n*-leucine has been effected by Fischer and Hagenbach (Ber. 1901, 34, 3764) by the fractional crystallisation of the cinchonine salt of the benzoyl derivative. The *benzoyl* derivative of racemic *n*-leucine has m.p. 134° (corr.); l-*benzoyl*-n-*leucine* crystallises with $\frac{1}{2}H_2O$, has m.p. 53° (corr.), and $[\alpha]_D^{20°}$ −21·9° in aqueous solution; lævo n-*leucine* prepared from this has $[\alpha]_D$ −22·4°; *d-benzoyl*-n-*leucine* has $[\alpha]_D$ +21·4°, and dextro n-*leucine* has $[\alpha]_D$ +21·3°. l-n-*Leucine picrolonate* softens at 145° and melts at 150°, it has $[\alpha]_D^{20}$ +19·6° (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127).

Marko (Annalen, 1908, 362, 333) has similarly separated *d*- and *l*- *n*-leucine from the racemic compound by crystallising the brucine salt of the formyl derivative of the racemic compound. *r-Formyl*-n-*leucine* has m.p. 113°–115° (corr.); *l-formyl*-n-*leucine* has m.p 115°–118·5° (corr.), and $[\alpha]_D^{20}-17{\cdot}56°$; *lævo* n-*leucine* has $[\alpha]_D^{20}-22{\cdot}99°$ *d-formyl*-n-*leucine* has $[\alpha]_D^{20}+17{\cdot}63°$, and yields *dextro* n-*leucine* $[\alpha]_D^{20}+23{\cdot}14°$.

ψ-Leucine has been obtained from the oxime of trimethylpyruvic acid $C_8H_{11}O_3N,H_2O$, by reduction with zinc dust and 50 p c. acetic acid or with aluminium amalgam in 50 p.c. alcohol; it forms hard laminar crystals that begin to sublime at 250°. The *naphthalenesulphonyl* derivative has m.p. 200–203°; the p-*toluenesulphonyl* derivative has m.p. 226°; and the *nitrate* has m.p. 151° (Knoop and Landermann, Zeitsch. physiol. Chem. 1914, 89, 157). M. A. W.

LEUCITE. A volcanic mineral consisting of potassium aluminium silicate $KAl(SiO_3)_2$, found as grey crystals with the external form of the cubic icositetrahedron (211). Optical examination of the crystals in thin sections shows them to be birefringent and to consist of a complex intergrowth of twin-lamellæ. At a temperature of 714° the material is optically isotropic and truly cubic, and in the red-hot lavas it, no doubt, grew as a cubic crystal. Sp.gr. 2 47; H. 5½. The mineral occurs abundantly as embedded crystals in the alkali-rich lavas of certain district e.g Vesuvius, Rome, the Eifel, and the Leucite Hills in Wyoming. Other localities are in Montana, Arkansas, Brazil, Sardinia, Bohemia, Trebizond in Asia Minor, Kilimanjaro in Africa, Cape Verde Islands, Java, Borneo, Celebes, New South Wales, Siberia. It is decomposed by hydrochloric acid, and is readily affected by weathering processes. Containing a considerable amount of potash (K_2O, 21·5 p.c.), attempts have been made to employ this mineral as a source of potassium salts and as a fertiliser. The leucite-bearing rocks of Wyoming contain K_2O 7·99–11·91 (average 10·74) p c., which is present partly in other minerals besides the leucite, such as mica and orthoclase (*v.* A. R. Schultz and W. Cross, Potash-bearing rocks of the Leucite Hills, Wyoming, Bull. U.S. Geol. Survey, 1912, No. 512). A review, with a full bibliography, of the many attempts that have been made to extract potash from the leucite lavas of Italy is given by H. S. Washington, Metall Chem. Engin. Jan. 15, 1918. L J. S.

LEUCOLINE. Syn. for Quinoline.

LEUCOMAÏNES *v.* Ptomaines.

LEUCOPYRITE *v.* Löllingite.

LEVANT SAPOTOXIN *v.* Glucosides.

LEVIGATION. Levigation is the mechanical process by which hard substances are reduced to a very fine powder by grinding them with water. The process is used principally in the preparation of pigments. On a small scale the substance is ground with a 'muller.' The muller is a piece of hard stone, convenient in shape and size to hold in the hand, and carefully flattened and polished on one side. The pigment to be ground is mixed with water on a large square slab of stone, preferably marble, and then ground with the muller. The finest artists' colours are ground in this way. On the large scale the pigment is first thoroughly mixed with water in a pug-mill. It is then ground between millstones similar to those used for flour, or under edge runners. Sometimes the millstones are replaced by three horizontal granite rollers, between which the pigment is ground. A mill with stones 2 feet in diameter will grind 15 cwt. of paint in 11 hours.

LEVULIN *v.* Dandelion root.

LEVULOSE, LÆVULOSE *v.* Carbohydrates. For the specific rotation of lævulose, *see* Vosburgh, J. Amer. Chem. Soc. 1920, 42, 1696.

LEVURARGYRE. Trade name for a mercury compound of nucleoprotein.

LEVURETIN, LEVURINOSE *v.* Synthetic drugs.

LIBAVIUS, FUMING LIQUOR OF. *Stannic chloride* $SnCl_4$ (*v.* Tin).

LICHENIN *v.* Iceland moss, art. Gums.

LICHENS. Many species have been employed from the earliest times in medicine, dyeing, and as foodstuffs (Mémoires sur l'utilité des lichens, par Hoffmann, Amoreux et Willemet, Lyon, 1787). From about the year 1300 certain species have been employed for the production of the purple dyestuff 'archil' or 'orchil,' as they contain colourless principles, derivatives of orcin, which under the influence of ammonia and atmospheric oxygen yield the purple colouring matters known as orcein (*v.* Archil). Under the name of *Crottle* or *Crotal*, with various descriptive prefixes, several species have been, and still are to a very limited extent, directly applied in dyeing buff and brown colours on homespun yarn in the Highlands of Scotland, Wales, &c. The dyestuff appears to be ready formed in the plant and is obtained by simple extraction. The best known are *Parmelia Saxatilis* or *Black Crottle*, and *P. omphalodes*, while others are *P. caperata*, or *Stone Crottle*, *P. ceratophylla* or *Dark Crottle*, *P. parietina*, and a few species of *Sticta*, especially *S. pulmonaria* or *Hazel Crottle*. These lichens undergo no preparation, being gathered in July or August, when they are richest in colouring matter, and simply dried in the sun. They dye without addition to the bath and do not form lakes. Fine shades of brown are obtained, fast to acids and alkalis, but less fast to light than a mixture of Melachrome Brown B, and Melachrome Orange 3R (Edge, J. Soc. Dyers and Col. 1914, 30, 186). Those lichens, e.g. Iceland moss (*Cetraria islandica*, Ach.), which serve as foodstuffs, contain a starch-like substance termed *lichenin*, which is capable of conversion into glucose.

Our earlier chemical knowledge of the constituents of many of these lichens is mainly due to the work of Knop, Rochleder, Heldt, Schunck, Schmidt, Stenhouse, Stenhouse and Groves, and Weppen, whereas for the later very numerous investigations we are chiefly indebted to the chemists Oswald Hesse and Wilhelm Zopf. As a result, a very large number of new compounds have been isolated and described, the constitutions of which in most cases, however, are as yet undecided. On the other hand, considerable advance has been made as regards the exact structure of some of the more common constituents, viz. atranorin (atranoric acid), barbatic acid, evernic acid, erythrin (erythric acid), lecanoric acid, and ramalic acid, and the chemistry of these substances is dealt with under their special headings.

As the work of Hesse (H.) is mainly to be found in the Journal für praktische Chemie, and that of Zopf (Z.) in the Annalen, to avoid frequent repetition the year only of the papers published in the journals is noted below. For further details, *see* Hesse, J. pr. Chem. 1911, [ii.] 83, 22.

Trachylia tigillaris (Fr.) (*Acolium tigillare*; *Calicium tigillare*, *Cyphelium tigillare*), rhizocarpic acid $C_{28}H_{20}O_7$ (H.), m.p. 177°–178°, and acolic acid (H. 1900).

Acarospora chlorophana, rhizocarpic acid, pleosidic acid $C_{17}H_{28}O_4$, m.p. 131°–132° (Z. 1903).

Alectoria implexa, Nyl. (*A. cana*), zeorin, salazinic acid (Z. 1898). *A. ochroleuca*, usnic acid $C_{18}H_{16}O_7$, and barbatic acid (Z. 1899). *A. sarmentosa*, usnic acid (Z. 1900). *A. jubata*, var. *implexa*, salazinic acid, alectoric acid $C_{28}H_{24}O_{15}$, m.p. 186°. *A. articulata*, *d*-usnic acid, usnaric acid $C_{30}H_{22}O_{15}$, m.p. 240°–260°. *A. canariensis*, *d*-usnic acid, usnaric acid (H. 1902). *A. implexa*, atranorin (H. 1906)

Anaptychia ciliaris, atranoric acid (atranorin). *A. speciosa*, atranorin, zeorin $C_{52}H_{88}O_4$ (Z. 1895–1897).

Aspicilia calcarea, erythric acid, oxalic acid, aspicilin, m.p. 178.5° (H. 1900). *A. calcarea*, var *farinosa*, erythrin, erythritol (H 1915). *A. gibbosa*, aspicilic acid m.p. 150° (H 1904)

Baeomyces roseus, an acid, m.p. 180° (H. 1898)

Biatora lucida, rhizocarpic acid $C_{28}H_{20}O_7$, atranorin (Z. 1897; H 1907): no usnic acid (*cp.* Knop, 1843). *B. mollis*, diffusic acid (Z. 1905). *B. Lightfootii*, *l*-usnic acid (Z 1906). *B. grandulosa*, gyrophoric acid $C_{16}H_{14}O_7$ (Z. 1906).

Blastenia arenaria (*Callopisma erythrocarpa*), phytosterol, blasterin, m.p. 170° (H 1898) *B. arenaria*, atranorin, gyrophoric acid $C_{16}H_{14}O_7$ (H. 1898). *B. Jungermanniae*, parietin (Z 1906)

Calycium chrysocephalum, vulpic acid (H. 1898; Z. 1895). *C. chlorinum* or *chlorellum*, vulpic acid (Z. 1895); pulvic acid and traces of leprarin $C_{19}H_8O_9$ (Kassner, Arch. Pharm. 239, 44; H. 1900). *C. flavum*, chrysocetraric acid $C_{19}H_{14}O_6$ (H. 1900). *C. Stenhammari*, calycin $C_{18}H_{12}O_5$ (Z. 1895).

Callopisma flavovirescens, chrysophanic acid, physcion $C_{16}H_{12}O_5$ (H. 1902). *C. vitellinum*, calycin (Z. 1895); callopismic acid and mannitol (Z. 1897).

Rhizocarpon oreites, A. Zahlbr. (*Catocarpus oreites*), rhizocarpic acid $C_{28}H_{20}O_7$, psoromic (parellic) acid $C_{21}H_{16}O_9$ (Z. 1905).

Cetraria cucullata (*Platysma cucullatum*), protolichesteric acid $C_{18}H_{32}O_5$ (Z 1902). *C. chlorphylla*, protolichesteric acid and atranorin (Z. 1902). *C. complicata*, protocetraric acid $C_{30}H_{22}O_{15}$, *l*-usnic acid, and atranorin.

Cetraria islandica contains starch not deposited in granules, but uniformly distributed among the cells (lichenin). The lichenin, which is convertible into sugar, is present in such large quantity that this lichen can be used for food (Schmidt, Annalen, 51, 29). There is also said to be present cetraric acid, lichenstearic acid (Knop and Schaedermann, Annalen, 55, 144), protocetraric acid, and proto-*α*-lichesteric acid (Z. 1902; H. 1903 and 1904), *α*-lichenostearic acid $C_{18}H_{30}O_5$ (m.p. 122°–123°), *β*-lichenostearic acid $C_{18}H_{30}O_5$ (m.p. 121°), *γ*-lichenostearic acid $C_{18}H_{30}O_5$ or $C_{19}H_{32}O_5$ (m.p. 121°–122°) paralichenostearic acid $C_{20}H_{34}O_5$, dilichenostearic acid $C_{36}H_{60}O_{10}$, and cetraric acid $C_{26}H_{20}O_{12}$ (H. 1898) contains no cetraric acid as such, it being formed during extraction. Carbohydrates are lichenin, *d*-lichenidin and lichenoin (H. 1916).

C. nivalis, usnic acid (Z. 1904); *l*-usnic acid, nivalic acid $C_{20}H_{26}O_6$; lichenin and *l*-lichenidin $C_{12}H_{22}O_{11}$ (H 1916). *C. stuppea* protolichesteric acid (Z. 1904), proto-*α*-lichesteric acid, dilichesteric acid, cornicularin and stuppeaic acid $C_{19}H_{26}O_4$ (H. 1911). *C. aculeata* or *Cornicularia aculeata*, protolichesteric acid (Z. 1904); lichenin and lichenic (fumaric) acid, acanthellin $C_{18}H_{31}O_5$, m.p. 188° (H. 1911). *C. pinastri*, pinastric acid $C_{10}H_8O_3$ (Z. 1895) *C. glauca* (*Platysma glaucum*), lichenin (Berzelius). *C. juniperina*, chrysocetraric acid $C_{19}H_{14}O_6$, usnic and vulpic acids (H. 1898). *C. pinastri*, chrysocetraric, usnic and vulpic acids (H. 1898; Z. 1899) *C. fahlunensis*, cetraric acid (Z. 1898).

Candelaria concolor, callopismic acid or ethylpulvic acid $C_{20}H_{16}O_5$, dipulvic acid C[illegible]$H_{22}O$[illegible] (Z.); calycin, and stictaurin $C_{18}H_{12}O_5$ (H.; Z 1899). According to Hesse, 1898, dipulvic acid is a mixture of calycin and pulvic anhydride. *C. vitellina*, stictaurin (Z. 1899), calycin and pulvic anhydride (Z. 1899).

Cladina silvatica, usnic acid and cetraric acid (Z. 1898). *C. alpestris*, usnic acid (Z. 1898). *C. rangiferina*, cetraric acid and atranorin (Z 1898) and usnic acid (H. 1898). *C. pyxidata*, parellic acid (H. 1898). *C. coccifera*, cocellic acid $C_{20}H_{22}O_7$ (K. 1898). *C. uncialis*, *d*-usnic and thamnolic acids $C_{20}H_{18}O_{11}$ (Z. 1902).

Cladonia amaurocraea, usnic acid (Z. 1898). *C. alcicornis*, usnic acid (H. 1902). *C. deformis*, usnic acid (Z. 1900). *C. cyanipes*, usnic acid (Z 1900). *C. Floerkeana*, cocellic and thamnolic acids (H. 1900). *C. rangiformis*, atranorin, rangiformic acid $C_{20}H_{33}O_5{\cdot}OMe$ (H. 1898). *C. uncinata* (no usnic acid, *see* Knop, Annalen, 1844, 49, 120); but uncinatic acid $C_{23}H_{28}O_9$ (H. 1900). *C. destricta* (*C. uncialis*), usnic acid and starch (Knop, Annalen, 49, 119); *l*-usnic acid (Salkowski, Annalen, 1901, 319, 391); *l*-usnic acid, cladestin (m.p. 242°–245°), squamatic acid, destritic acid, destrictasic acid, and cladestic acid $C_{15}H_{24}O_2$ (H. 1911). *C. incrassata*, *l*-usnic acid (S.). *C. glauca*, squamatic acid (Z. 1902). *C. strepsilis*, thamnolic acid and strepsilin (Z. 1903). *C. thamnolis*, thamnolic acid $C_{20}H_{18}O_{11}$, and strepsilin. *C. destricta*, *l*-usnic acid (Z. 1903); *l*-usnic and squamatic acids and cladestin (H. 1904). *C. macilenta*, usnic acid and starch (Knop, *l.c.*); rhizonic acid (Z. 1903); coccellic acid, thamnolic acid, rhodocladonic acid (H. 1915). *C. squamosa*, var. *ventricosa*, squamatic acid (Z. 1904). *C. squamosa*, var. *denticollis*, squamatic acid (Z. 1907). *C. fimbriata*, var. *simplex*, fumaroprotocetraric acid and fimbriatic acid (Z. 1907). *C. fimbriata*, var *cornuto-radiata*, fumaroprotocetraric acid (Z. 1907); no confirmation of this; probably [illegible] acid (H. 1915). *C. pityrea*, var. *cladomorpha*, fumaroprotocetraric acid (Z. 1907). *C. silvatica*, var. *condensata*, *l*-usnic acid (Z. 1907), cornicularin $C_{23}H_{44}O_5$ (H. 1915). *C. verticillata*, var. *subcervicornis*, fumaroprotocetraric acid (Z. 1907), atranorin and cervicornin. *C. chlorophæa*, fumaroprotocetraric acid. *C. gracilis*, var. *chordalis*, fumaroprotocetraric acid (Z. 1907). *C. crispata*, var. *gracilescens*, squamatic acid (Z. 1907);

cladonin $C_{30}H_{41}O_6$ (H. 1915). *C. coccifera*, cocellic acid $C_{20}H_{22}O_7$ (H. 1895). *C. incrassata*, *l*-usnic acid (Z. 1905). *C. rangiferina*, usnic acid (Rochleder and Heldt, Annalen, 48, 2); lichenin (Schmidt, *ibid.* 51, 29); cladonic acid (β-usnic acid) $C_{18}H_{18}O_7$ (Stenhouse, *ibid.* 155, 58); *d*-usnic acid (no *l*-usnic) and silvatic acid $CO_2Me{\cdot}C_{18}H_{34}O_3{\cdot}COOH$ (H. 1907); atranorin and fumaroprotocetraric acid (Z. 1906). *C. rangiferina*, var. *vulgaris*, atranorin and protocetraric acid (H. 1898). *C. rangiferina*, var. *silvatica*, *d*-usnic acid (Z. 1906); usnic and protocetraric acids (H. 1898). *C. tenuis*, fumarprotocetraric acid and *d*-usnic acid (H 1915). *C. pyxidata*, lichenin (Schmidt, Annalen, 51, 29); emulsin (Hérissey, J. Pharm. Chim. 1898, [vi.] 7, 577).

Cornicularia aculeata, rangiformic acid (H. 1902). *C. aculeata*, var. *stuppea*, cornicularin C_{2}[illegible]$H_{14}O_5$ (H. 1915) *C. aculeata*, var. *acanthella*, dimannitol (H. 1915).

Chiodecton sanguineum (*C. rubrocinctum*), chiodectonic acid $C_{14}H_{18}O_5$.

Cyphelium trichiale, var *candelare*, calycin (Z. 1906).

Darbishirella gracillima, parellic acid (H. 1898).

Dendrographa leucophaea, protocetraric acid (H. 1898); erythrin and orcinol (Ronceray, Bull. Soc. chim. 1904, [iii.] 31, 1097).

Dimelaena oreina, zeorin and usnic acid (Z. 1897)

Diploicia canescens (*Catolechia canescens*), diploicin, m.p. 225°, catolechin, m.p. 214°–215°, and atranorin (Z. 1904).

Diploschistes scruposa, diploschistessic acid $C_{15}H_{16}O_7$ (Z. 1906).

Endocarpon miniatum (α) *vulgare*, phytosterol and an acid (H. 1898).

Evernia divaricata, divaricatic acid (H. 1900) $C_{21}H_{24}O_7$, and usnic acid (Z. 1897); no usnic acid (H. 1911). *E. furfuracea*, usnic acid (Rochleder and Heldt, Annalen, 48, 9); no usnic acid, but erythric acid (Z. 1897), or rather olivetoric acid $C_{27}H_{36}O_8$ (Z. 1900), physodic acid, physodylic acid $C_{21}H_{26}O_8$, and furevernmic acid (H. 1907); atranorin, evernuric acid $C_{22}H_{21}O_8$, and furevernic acid, but no erythric or olivetoric acids (H. 1906); emulsin (Hérissey, J. Pharm. Chim. 1898, [v.] 7, 577). *E. prunastri*, evernic acid, atranorin (Z. 1897); evernic acid, usnic acid, and atranorin, and chrysocetraric acid (H. Annalen, 1895) $C_{19}H_{14}O_6$: atranorin and evernic acid when grown on birch, limes, beech, sandstone; usnic acid in addition when on oak (H. 1915). *E. thamnodes*, divaricatic acid, usnic acid (Z. 1897; H. 1900). *E. vulpina*, vulpic acid and atranorin (H.). *E. illyrica* (Dalmatia), divaricatic acid and atranorin (Z. 1904). *E. ochroleuca*, usnic acid (Knop, Annalen, 49, 122).

Everniopsis Trulla, salazinic acid and atranorin (Z. 1897).

Gasparrinia medians (*Physcia medians*) calycin, rhizocarpic acid (H. 1898); pulvic lactone (H. 1903). *G. sympagea*, parietin (Z. 1905). *G. elegans* (*Physcia elegans*), physcion (H. 1898). *G. murorum*, physcion (H. 1898). *G. decipiens* physcion (H. 1898). *G. cirrhochroa*, chrysophanic acid (Z. 1897).

Graphis scripta, salazinic acid (H. 1900).

Gyalolechia aurella, calycin (Z. 1895), callopismic acid (Z. 1897), stictaurin (Z. 1899).

Umbilicaria pustulata (Hoffm.) (*Gyrophora pustulata*), gyrophoric acid $C_{36}H_{36}O_{15}$ (Stenhouse, Annalen, 70, 218) $C_{16}H_{14}O_7$ (H.). *G. hirsuta*, gyrophoric acid (Z. 1898). *G. deusta*, gyrophoric acid (Z. 1898). *G. polyphylla*, umbilicaric acid $C_{25}H_{22}O_{10}$ (Z. 1898); umbilicaric acid and gyrophoric acid (H. 1898, 1901). *G. hyperborea*, umbilicaric acid (Z. 1898). *G. deusta*, umbilicaric acid (Z. 1898). *G. vellea*, gyrophoric acid and gyrophorin, m.p. 189° (Z. 1899). *G. spodochroa*, var. *depressa*, gyrophoric acid (Z. 1900). *G. polyrrhiza*, umbilicaric acid, lecanoric acid, gyrophoric acid (Z. 1905).

Hæmatomma ventosum, divaricatic acid $C_{22}H_{26}O_7$, m.p. 149° (Z. 1898); *d*-usnic acid, divaricatic acid, and an acid resembling alectoric acid (H. 1900). *H. coccineum*, var. *leiphæmum*, leiphæmin, m.p. 193°, atranorin, zeorin (Z. 1902). *H. coccineum*, var. *abortivum*, coccic acid $C_{12}H_{16}O_{10},3H_2O$, m.p. 262°–[illegible]; atranorin, hæmatommin $C_{10}H_{16}O$ or $C_{20}H_{32}O_2$, m.p. 143°–144°, and hæmatommidin, m.p. 194°–196° (Z. 1903); no zeorin (H. 1907). *H. coccineum*, var. (?), lecanoric acid (H. 1907). *H. coccineum*, var. (?) (from Wildbad), coccic acid, atranorin, zeorin, hydrohæmatommin $C_{10}H_{18}O$, m.p. 101° (H. 1906). *H. coccineum*, *l*-usnic acid, zeorin, atranorin, porphyrilic acid, hymenorhodin, and leiphæmin (Z. 1906). *H. leiphæmum*, atranorin, zeorin, leiphæmin, leiphæmic acid $C_{22}H_{46}O_5$, m.p. 114°–115° (Z. 1903). *H. porphyrium*, atranorin, zeorin, porphyrilic acid, leiphæmin, hymenorhodin (Z 1906).

Pertusaria dealbata, Nyl. f. *corallina*, Cromb. (*Isidium corallinum*) ('white crottle'), calcium oxalate (Braconnot, Ann. Chim. Phys. [ii.] 28, 319).

Lecanora atra, atranoric acid (atranorin) $C_{19}H_{18}O_8$, and a yellow crystalline substance (Paternò and Oglialoro, Gazz. chim. ital. 1877, 7). Hesse (Ber. 10, 1324) considers the atranoric acid to be hydrocarbonusnic acid, and the yellow substance to be cladonic acid. Obtained from certain districts it contains lecanorol (Z. 1897) $C_{27}H_{30}O_9,H_2O$. *L. varia*, psoromic acid and *l*-usnic acid (Z. 1905). *L. grumosa*, atranorin and lecanorol (Z. 1897). *L. cenisea*, atranorin and roccellic acid $C_{17}H_{32}O_4$ (*cp.* Schunck and Hesse, *Roccella tinctoria*). *L. sordida*, atranorin, zeoric acid (Z. 1897). *L. sordida*, var. *glaucoma*, atranorin and parellic acid (H. 1898). *L. sordida*, var. *Swartzii*, atranorin, thiophanic acid $C_{12}H_6O_{12}{\cdot}H_2O$, m.p. 242°, roccellic acid, lecasteric acid $C_{10}H_{20}O_4$, m.p. 116°, and lecasteride $C_{10}H_8O_3$, m.p. 105° (H. 1898). *L. campestris*, atranorin (Z. 1897). *L. badia*, stereocaulic acid (Z. 1897). *L. effusa*, atranorin and usnic acid (Z. 1897). *L. subfusca*, atranorin (Z. 1897; H. 1900). *L. epanora*, zeorin and lepanorin, m.p. 131°–132° (Z. 1900). *L. glaucoma* (*L. sordida α-glaucoma*) (from Tyrol), atranorin, thiophanic acid, roccellic acid (Z. 1903). *L. sulphurea*, usnic acid (Z. 1903). *L. parella* ('light crottle'), parellic acid, lecanoric acid (Schunck, Annalen, 54, 257, 274; 41, 161). *L tartarea* (Linn.) (*Patellaria tartarea*, *Parmelia tartarea*), erythric acid, synonymous with Nees. v. Esenbeck's 'remarkable resin' (Brandes' Archiv. Apoth. 16, 135), with Heeren's erythrin, and with Kane's erythrilin (Schweigger's, J., Ch. Phys. 59, 313). Schunck found crustaceous lichens belonging to *Lecanora*, &c., collected on the basalt rocks of the Vogelsberg in Upper Hessia to contain lecanoric and erythric acids (Annalen, 41, 157). In a specimen from Norway, Stenhouse (*ibid.* 70, 218) found gyrophoric acid. *L. ventosa*, usnic acid (Knops, *ibid.* 49, 122).

Rhizocarpon geographicum, Dl. (*Lecidea geographica*) usnic acid (Knop, *l.c.*). *Lecidea candida* (*Psora candida*), calcium oxalate (Braconnot, Ann. Chim. Phys. [ii.] 28, 319). *L. cineroatra*, lecidic acid $C_{25}H_{27}O_4·COOMe$, m.p. 147°, and lecidol, m.p. 93° (H. 1898). *L. sudetica*, salazinic acid (Z. 1899). *L. confluens*, confluetin, m.p. 147°–148° (Z. 1899). *L. grisella*, gyrophoric acid (H. 1900). *L. aglaotera* (*L. armeniaca*, var. *lutescens*), roccellic and cetraric acids (Z. 1904).

Lepraria latebrarum, leprarin, m.p. 155°, roccellic acid (Z. 1897), and atranorin (Z. 1900); *d*-usnic, hydroroccellic, leprarie, and talebraric acids (m.p. 208°) and atranorin (H. 1903). *L. flava*, calycin, pinastric acid, calyciarin (Z. 1905) *L. xanthina* (from Vorarlberg), physcion (H. 1906). *L. latebrarum* (Baden-Baden), atranorin, leprarinic acid, oxyroccellic acid, and neobraic acid (H. 1906). *L. candelaris*, calycin (Z. 1906). *L. chlorina*, calycin (Z. 1895).

Lepra candelaris (*Lepraria flava*), calycin

$$C_{18}H_{11}O_4·OH,$$

m.p. 240°–242° (H. 1898).

Leprantha impolita (*Arthonia pruinosa*), lecanoric acid, leprantin $C_{25}H_{10}O_{10}$, m.p. 183°, leprantháic acid $C_{20}H_{32}O_2$, m.p. 111°–112° (Z. 1904).

Mycoblastus sanguinarius, caperatic acid and atranorin (Z. 1899).

Menegazzia pertusa (*Parmelia pertusa*), atranorin and farinacic acid (capraric and pysodic acids absent) (H. 1907).

Nephroma arcticum, zeorin, nephrin, and *d*-usnic acid (Z. 1909). *N. antarcticum*, zeorin and *d*-usnic acid (Z. 1909). *N. parile*, zeorin and mannitol (Z. 1909). *N. resupinatum*, mannitol (Z. 1909). *N. lævigatum*, mannitol (Z. 1909). *Nephromium lævigatum*, usnic acid and nephrin $C_{20}H_{32},H_2O$, m.p. 168° (H. 1898). *N. tommentosum*, usnic acid and nephrin (H. 1898). *N. lusitanicum*, nephrin and nephromin $C_{16}H_{12}O_6$, m.p. 196° (H. 1898).

Ochrolechia androgyna (*Lecanora subtartarea*), gyrophoric acid and calyciarin (Z. 1905). *O. pallescens*, var. *parella* (from Auvergne), parellic acid and ochrolechiasic acid $C_{22}H_{11}O_9$, m.p. 282° (K. 1906); but no lecanoric acid (*see* Schunck, Annalen, 1845, 54, 274) (Z. 1898). *O. tartarea*, gyrophoric acid (Z. 1898).

Pannaria lanuginosa, hydroxyroccellic acid $C_{17}H_{32}O_5$, m.p. 128°, and pannaric acid $C_9H_8O_4$, m.p. 224° (H. 1901).

Parmelia aleurities, atranorin (Z. 1897). *P. tiliacea*, atranorin and parmelialic acid, m.p. 165° (Z. 1897); the latter is in reality lecanoric acid (H. 1898 and 1900). *P. perlata*, atranorin and hæmatommic acid (Z. 1897); usnic acid, lecanoric acid, and perlatin (H. 1900); imbricaric acid (Z. 1902); no lecanoric acid (H. 1903); atranorin and perlatic acid $C_{27}H_{27}O_9·OMe,2H_2O$ (H. 1904). *P. perlata* from certain sources: (*a*) atranorin, (*b*) atranorin, usnic, and vulpic acids, (*c*) atranorin and lecanoric acid, (*d*) atranorin and perlatin $C_{19}H_{14}O_5(OMe)_2$ (H. 1898). *P. saxatilis*, stereocaulic acid and salazinic acid. Latter chief dyeing constituent (Ryan and O'Riordan, Proc. Roy. Irish Acad. 1917, 33, 911). *P. saxatilis*, var. *sulcata*, atranorin and stereocaulic acid (Z. 1897); protocetraric acid only (H. 1900), not protocetraric but pannatic acid (H. 1904); usnic acid (Schmidt, Annalen, 51, 29). *P. saxatilis*, var. *panniformis*, atranorin, protocetraric acid, and usnetic acid $C_{24}H_{26}O_8$ (not $C_9H_{10}O_3$), m.p. 192° (H. 1900). *P. saxatilis retiruga*, atranorin, protocetraric acid, and saxatic acid $C_{25}H_{40}O_8$, m.p. 115° (H. 1903), parmatic acid and not protocetraric acid (H. 1916). *P. physodes* (or *P. ceratophylla*, var. *physodes*) is known as 'dark crottle,' and is employed for dyeing a brown colour on homespun woollen yarn. Contains physodin and two colourless substances (Gerding, Brandes, Arch. Pharm [ii.] 87, 1), ceratophyllin (H. Annalen, 119, 365), atranorin, physodalic acid, and physodalin (Z. 1897 and 1898); evernuric acid, physodylic acid, capraric acid, and atranorin (H. 1907). *P. parietina*, chrysophanic acid (Rochleder and Heldt, 48, 12); identical with Thomson's (Edin. New. Phil Jour. 37, 187), parietin, also (H. 1895) physcion $C_{16}H_{12}O_5$, physcianin $C_{10}H_{12}O_4$, m.p. 143°, and physciol $C_7H_8O_3$, m.p. 107°. A variety of *P. parietina* growing on sandstone rock and not on trees like that of Rochleder and Heldt, contained vulpic acid (chrysopicrin) Stein (J. pr. Chem. [i.] 93, 366). *P. caperata* ('stone crottle'), emulsin (Hérissey, J. Pharm. [vi.] 7, 577); capraric acid $C_{22}H_{18}O_8(COOH)_2$, m.p. 240°, usnic acid, caperatic acid $COOMe,C_{18}H_{33}O_2(COOH)_2$, m.p. 132°, and caperin $C_{36}H_{60}O_3$, m.p. 243° (H. 1898), *d*-usnic acid (H. 1900), specimens from oaks contain caperin and caperidin in addition (H. 1915). *P. caperata* from *Castanea vesca*, usnic, capraric and caperatic acids (H. 1904). *P. conspersa*, usnic acid, zeorin, and atranorin (Z. 1898), usnic acid and salazinic acid (H. 1898); *d*-usnic acid and conspersaic acid, m.p. 252° (H. 1903). *P. acetabulum*, atranorin (Z. 1898); atranorin and salazinic acid (H. 1901). *P. excrescens*, zeorin and atranorin (Z. 1898). *P. perlata*, var. *ciliescens*, atranorin (Z. 1898). *P. Nilgherrensis*, atranorin (Z. 1898). *P. perforata*, zeorin and atranorin (Z. 1898); lecanoric acid (H. 1900). *P. olivetorum*, atranorin (Z. 1898); lecanoric acid, but no erythric acid (H. 1900); olivetoric acid $C_{27}H_{34}O_8$, m.p. 141°–142°, (Z. 1902); atranorin, olivetorin, m.p. 143°, and olivetoric acid $C_{21}H_{26}O_7$ (H. 1903). *P. pertusa*, physodalic acid (Z. 1898). *P. fuliginosa*, atranorin and lecanoric acid (H. 1898). *P. fuliginosa*, var. *ferruginascens*, lecanoric acid (Z. 1899). *P. pulverulenta*, unknown acid (H. 1898). *P. ciliaris*, evernnic acid and atranorin (?) (H. 1898) *P. omphalodes* (*P. saxatilis*, var. *omphalodes*). Under the name of 'black crottle' this lichen is employed for dyeing a brown colour in the outer Hebrides (Lewis and Harris); contains stereocaulic acid (Z. 1899), atranorin, usnetic acid, parmatic acid and (Knop's) lobaric acid (?) (H. 1916). *P. tiliacea*, var. *scortea*, lecanoric acid (Z. 1899). *P. verruculifera*, lecanoric acid (Z. 1899). *P. glomellifera*, glomelliferin, m.p. 143°–144° (Z. 1899 and 1902). *P. incurva*, usnic acid (Z. 1900). *P. Borreri*, lecanoric acid (Z. 1900). *P. sorediata*, diffusin (Z. 1900); lecanoric acid (H. 1900). *P. tinctorum*, atranorin (H. 1900). *P. tinctorum* (E. Africa), atranorin and lecanoric acid (H. 1906). *P. tinctorum* (Madras cinchona bark), atranorin and lecanoric acid (H. 1904). *P. glabra*, lecanoric acid (H. 1902). *P. lacarnensis*, imbricaric acid (Z. 1902). *P. sinuosa*, *d*-usnic and usnaric acids (Z. 1902).

Parmelia cetrata (Java cinchona bark), cetrataic acid $C_{29}H_{24}O_{14}$, m.p. 178°–180° (H. 1903). *P. olivacea*, oliveacein $C_{17}H_{22}O_6 \cdot H_2O$, m.p. 156°, and oliveaceic acid $C_{16}H_{19}O_5 \cdot OMe$, m.p. 138° (H. 1903). *P. revoluta*, atranorin and gyrophoric acid (Z. 1905). *P. pilosella*, atranorin and pilosellic acid, m.p. 245° (Z. 1905). *P. Mougeotii*, *d*-usnic acid (H. 1906).

Peltigera apthosa, peltigerin $C_{21}H_{20}O_8$ (or $C_{16}H_{16}O_6$), m.p. 170°–180°, and mannitol (Z. 1909). *P. malacea*, peltigerin, zeorin, and mannitol (Z. 1909). *P. horizontalis*, peltigerin, zeorin, and mannitol (Z. 1909). *P. polydactyla*, peltigerin mannitol, polydactylin, m.p. 178°–180°, and peltidactylin, m.p. 237°–240°. *P. venosa*, peltigerin. *P. scabrosa*, peltigerin. *P. propagulifera*, peltigerin and zeorin. *P. lepidophora*, peltigerin. *P. praetextata*, mannitol. *P. rufescens*, mannitol. *P. spuria*, mannitol. *P. canina*, caninin (Z. 1909); emulsin (Hérissey, J. Pharm. Chim. [vi.] 7, 577)

Pertusaria lichens on beech contain picrolichenin and salazinic acid, on oak contains no picrolichenin (H. 1916). *Pertusaria amara* (*P. communis β-variolosa*, *Variolaria amara*), emulsin (Hérissey, *l.c.*), cetraric acid, pertusaric acid $C_{24}H_{38}O_6$, m.p. 103°, pertusarin $C_{30}H_{50}O_2$, m.p. 235°, pertusarene $C_{60}H_{100}$, m.p. 286°, and pertusaridin (H. 1898); salazinic acid and picrolichenin (Z. 1900); orbiculatic acid $C_{22}H_{36}O_7$ (H. 1901). *P. lactea*, lecanoric acid and variolaric acid, m.p. 285 (Z. 1902). *P. lactea* (sterile Auvergne), lecanoric acid and ochrolechiasic acid (H. 1906). *P. corralina* (*P. ocellata β-coralline*), ocellatic acid $C_{20}H_{15}O_{11} \cdot OMe$, m.p. 208° (H. 1901). *P. rupestris* (*P. communis β-areolata*), areolatin $C_{11}H_7O_6 \cdot OMe$, m.p. 270°, areolin, m.p. 243°, and gyrophoric acid $C_{16}H_{14}O_7$ (H. 1903). *P. glomerata* (Wildbad), porin $C_{42}H_{67}O_9OMe$, m.p. 166°, and porinic acid $2[C_{11}H_{12}O_4],H_2O$, m.p. 218° (H. 1903). *P. Wulfenii* (*P. sulfurea*, *P. sulphurella*, *P. fallax*), thiophanic acid (Z. 1904). *P. lutescens*, thiophanic acid (Z. 1904). *P. ocellata variolosa*, atranorin and gyrophoric acid $C_{32}H_{21}O_{14}$ (H. 1916).

Placodium gypsaceum, squamaric acid and usnic acid (Z. 1898); parellic acid, but no usnic acid (H. 1901). *P. chrysoleucum*, usnic acid (Z. 1898). *P. saxicolum*, var. *vulgare*, usnic acid and zeorin (Paternò, Atti. R. Accad. Lincei, 1876, [ii.] 3); zeorin, but no atranorin (H. 1898), *d*-usnic acid (H. 1900). *P. saxicolum*, var. *compactum*, atranorin (H. 1901). *P. melanaspis*, atranorin (Z. 1898). *P. Lagascæ*, psoromic and usnic acids (Z. 1897)..

Placodium crassum, atranorin (trace), *l*-usnic acid (H. 1901). *P. circinatum* (*α*) *radiosum*, salazinic acid (H. 1902).

Physcia ciliaris, emulsin (Hérissey, J. Pharm. Chim. [vi.] 7, 577). *P. endococcina*, zeorin and atranorin (Z. 1895), rhodophyscin and endococcin (Z. 1905). *P. caesia*, zeorin and atranorin (Z. 1895); atranorin and zeorin (H. 1902). *P. stellaris, f. adscendens*, atranorin (Z. 1895). *P. parietina*, atranorin and placodin, m.p 245° (H. 1899). *P. parienta*, physcione (frangula-emodin mono methyl ether (Ryan and O'Riordan, *l c.*). *P. medians*, vulpic acid and calycin (Z. 1895), calycin and callopismic acid (Z. 1897) *P. pulverulenta*, var. *β-pityrea*, atranorin (Z. 1895)

Physcia tenella, atranorin (Z. 1895). *P. aipolia*, atranorin (Z 1895).

Cetraria glauca (*Platysma glaucum*) atranorin and caperatic acid (Z. 1899). *Cetraria cucullata* (*P. cucullatum*), lichenostearic acid and usnic acid (Z. 1899). *P. diffusum*, diffusin, m.p. 135°–136°, and usnic acid (Z. 1899).

Pleopsidium chlorophanum, rhizocarpic acid (Z. 1895).

Pseudevernia ericetorum, atranorin, physodalin (Z. 1905) *P. olivetorina* (*Evernia furfuracea*, var. *olivetorina*), atranorin and olivetoric acid (H. 1911); olivoric acid $C_{23}H_{28}O_8$ and apo-olivoric acid (H. 1916).

Psora ostreata, lecanoric acid (Z. 1899).

Pulveraria chlorina, calycin, vulpic acid, and leprarin acid, m.p 228° (H. 1898). *P. latebrarum*, atranorin, parellic acid, latebride, m.p. 128°, and pulverin, m.p. 262° (H. 1898). *P. farinosa*, oxyroccellic acid, and pulveraric acid, m.p. 234° (H. 1898).

Pycnothelia (*Cladonia*) *papillaria*, var. *molariformis*, atranorin, cladonin and proto-*α*-lichestearic acid (H. 1915).

Raphiospora flavovirescens, rhizocarpic acid (Z 1895).

Ramalina calicaris, var. *fastigiata*, contains large quantities of starch (lichenin) and a small quantity of saccharic acid (Berzelius, Scherer's Annalen, 3, 97), usnic acid (Rochleder and Heldt, *ibid.* 48, 9). *R. calicaris*, var. *fraxinea*, lichenin and usnic acid (R. and H. *l.c.*); *α*-usnic acid (Hesse, Annalen, 117, 297). *R. ceruchis*, usnic acid and usnaric acid (H. 1898). *R. armorica*, atranorin, armoricaic acid, m.p. 240°–260°, armoric acid $C_{18}H_{18}O_7,H_2O$, m.p. 226°–228° (H 1907). *R cuspidata*, cuspidatic acid $C_{16}H_{20}O_{10}$, m.p. 218° (H. 1900), *d*-usnic acid (Ryan and O'Riordan, *l.c.*). *R. farinacea*, *d*-usnic acid and ramalic acid $C_{30}H_{26}O_{15}$, m.p. 240°–245° (H. 1903). *R. subfarinacea*, *d*-usnic acid and salazinic acid (Z. 1907). *R. minuscula*, *d*-usnic acid (Z. 1907). *R. Kullensis*, *d*-usnic acid, kullensisic acid $C_{22}H_{18}O_{12}$ (Z. 1907). *R. obtusata*, *d*-usnic acid, ramalinellic acid, m.p. 169°, and obtusatic acid (Z. 1907). *R. Landroensis*, *d*-usnic acid and landroensin (Z. 1907). *R. pollinaria*, ramalic acid $C_{16}H_{13}O_4OMe$ and evernic acid (Z. 1897): usnic acid, atranorin, evernic acid, and ramalic acid (H. 1898). *R. fastigiata*, emulsin (Hérissey, J. Pharm. Chim. 1898, [vi.] 5, 577) *R. fraxinea*, emulsin (Hérissey, *ibid.*). *R. polymorpha*, usnic acid (Z. 1897). *R. scopulorum* (*see* Thomson, Annalen, 53, 252), *d*-usnic acid, scopuloric acid $C_{19}H_{18}O_9$, m.p. 260° (Z. 1907). *R. thrausta*, usnic acid (Z. 1900). *R. yemensis*, *d*-usnic acid (H. 1902).

Reinkella birellina, roccellic and oxyroccellic acids (H. 1898).

Rhizocarpon geographicum f. contiguum, parellic acid, rhizonic acid $C_{19}H_{20}O_7$, m.p. 185°, rhizocarpic acid $C_{28}H_{22}O_7$ (H. Ber 1898, 31, 663), rhizonic acid is OMe·$C_{17}H_{14}O_2(OH)_2COOH$ (H.). *R. geographicum f. lecanorinum*, rhizocarpic acid (Z. 1895); parellic acid, rhizocarpinic acid, m.p. 156°, rhizocarpic acid

$$COOH \cdot C_{24}H_{16}O_3 \cdot COOEt$$

m.p. 177°–178°. Parellic acid

$$COOMe \cdot C_{17}H_{11}O_3(COOH)_2$$

m.p. 262°–265°, is the same as Zopf's psoromic acid, and the squamaric acid and zeoric acid of other writers (H.). *R. geographicum f. geronticum*, parellic and rhizocarpic acids, but not rhizocarpinic acid (H. 1909).

Rhizoplaca opaca (*Lecanora chrysoleuca, β-opaca, Parmelia rubina β-opaca, Squamaria chrysoleuca β-opaca*), usnic acid, placiodilic acid (previously termed placiodilin), and rhizoplacic acid $C_{21}H_{40}O_5$, m.p. 94°–95° (Z. 1905), usnic acid and placiodilic acid $C_{17}H_{18}O_7$, m.p. 156°–157° (Z. 1906).

Roccella fuciformis (*R. tinctoria*, var. *fuciformis*). This well-known 'orchella weed' is imported from Angola, Zanzibar, Madagascar, Ceylon, and Lima for the purpose of manufacturing archil and cudbear. It contains erythric acid (Heeren's erythrin, Kane's erythrilin) and roccellic acid (Schunck, Pharm. J. [iii.] 39, 164; Annalen, 61, 64; Kane, Trans. Roy. Soc. 1840, 273: Heeren and Schweiggers, J. Pharm. Chim 59, 346) Stenhouse (Annalen, 149, 288) examined a Lima weed in 1848, and found it to contain lecanoric acid, but this was probably *R. tinctoria* and not identical with the *R. fuciformis* examined by him in 1869, and in which he found erythric acid. Compare Hesse (Annalen, 117, 329, and 139, 22) who found Lima weed to contain erythric acid, but not lecanoric acid Stenhouse considers the *R. Montagnei* from Angola, in which he found erythric acid to be identical with *R. tinctoria*, var. *fuciformis*, examined by Schunck. A stunted variety of *R. fuciformis*, examined by Menschutkin and Lamparter, contained *β*-erythrin. In a better growing specimen erythrin was obtained (Lamparter, Annalen, 134, 243). A variety of *R. fuciformis*, probably from the west coast of Africa, contained erythric acid and a bitter substance picroroccellin (Stenhouse and Groves, *ibid*. 185, 14). More recently Hesse (1898) has found the weed to contain erythric acid and oxyroccellic acid.

Roccella Montagnei, erythric acid and oxyroccellic acid (H. 1898), orcinol (Ronceray, Bull. Soc. chim. 1904, iii. 1097). *R. fruticosa*, erythric acid (erythrin) (H. Ber. 1904, 37, 4693). *R. phycopsis* (Crete), erythrin, oxyroccellic acid, oxalic acid, and erythritol (H. 1906). *R. peruensis* (*R. fructectosa* and *R. cacticola*), erythrin, oxyroccellic, and roccellic acids (H. 1898), erythrin, erythritol, and oxalic acid (H. 1906). *R. portentosa*, lecanoric acid (H. 1898). *R. decipiens*, lecanoric acid (H. 1898). *R. sinensis*, lecanoric acid (H. 1898).

Roccella tinctoria. This lichen used largely for the manufacture of orchil and cudbear, is imported from the Cape of Good Hope, the Cape Verde Islands, and Chile (Valparaiso Weed). Formerly it seems to have been imported also from Lima (Stenhouse). It contains lecanoric acid (Stenhouse's *α*- and *β*-orsellic acid) and roccellinin. The latter is, however, probably a decomposition product of the former (Stenhouse, Annalen, 68, 55; 149, 288; Phil. Mag. [iii.] 32, 300). According to Hesse (1898) it contains erythrin, oxyroccellic acid, roccellic acid, and lecanoric acid, whereas Ronceray (Bull. Soc. chim. 1904, [iii.] 31, 1097) detected in this lichen the presence of lecanoric acid and orcinol (*cp.* Hesse, Ber. 1904, 37, 4693).

Roccellaria intricata, zeorin and roccellaric acid, m.p. 110° (H. 1898).

Squamaria elegans (*Gasparrinia elegans*), chrysophanic acid (Thomson, Phil. Mag. [iii.] 25, 39); physcion (H.).

Solorina crocea, soloric acid, m.p. 199°–201° (Z. 1895); solorinic acid, hydrosolorinol and mannitol (H. 1915).

Sphærophorus fragilis, sphærophorin, m.p. 138°–139°, and fragilin (Z. 1898), sphærophorin $(C_{14}H_{16}O_4)_n$, or $C_{28}H_{34}O_8$, sphærophoric acid, m.p. 206°–207°, and fragilin (Z. 1905).

Sphyridium placophyllum, atranorin (Z. 1898).

Stereocaulon alpinum atranorin, and stereocaulic acid, m.p. 200°–201° (Z. 1895). *S. corallöides*, atranorin and psoromic acid (Z. 1895), usnetic acid, atranorin, and an acid not psoromic acid. Zopf's stereocaulic acid from *S. alpinum* is usnetic acid (H. 1900). *S. incrustatum*, atranorin and psoromic acid (Z. 1895). *S vesuvianum*, psoromic acid (Z. 1895). *S. denudatum*, var. *genuinum* atranorin (Z. 1895). *S. tomentosum*, atranorin (Z. 1895). *S. pileatum*, atranorin and stereocaulic acid (Z. 1895 and 1899) *S. condensatum*, atranorin (Z. 1895). *S paschale*, atranorin (Z. 1895). *S. virgatum* f. *primaria*, atranorin (Z. 1895) *S. ramulosum*, atranorin (Z. 1895). *S. salazinum*, salazinic acid, which blackens at 260°–262° (H. 1900). Stereocaulic acid appears to be identical with stictaic acid (Bargellini and Monocada, Gazzetta, 1921, 51, ii. 173)

Sticta fuliginosa, trimethylamine (Z. 1897). *S. aurata*, stictaurin a derivative of pulvic acid (Z. 1899). Stictaurin has the formula $C_{18}H_{12}O_5$ (H 1900) *S desfontainii*, calycin and ethylpulvic acid (H 1900). *S pulmonaria*, stictaic acid $C_{19}H_{14}O_9$, m.p. 264°, stictinic acid (Knop and Schnedermann, J. pr. Chem. 1846, 39, 365), and not protocetraric acid (H 1900). This lichen is known as 'hazel crottle.'

Stictina gilva, stictinin, m.p. 160°–161° (Z. 1905).

Thamnolia vermicularis, thamnolic acid, m.p. 202°–204° (Z., Chem. Zentr. 1893, ii. 54). According to Hesse this has the formula $C_{19}H_{15}O_{10}\cdot OMe$ (1898 and 1900).

Thallœdema candidum, probably lecanoric acid (H. 1898).

Thalloschistes flavicans, parietin (Z. 1905) (Brittany); physcion and acromelin (H. 1907).

Tornabenia chrysophthalma, physcion (H. 1907). *T. flavicans*, var. *crocea*, physcion (H. 1907). *T. flavicans*, var. *acromela* (*Physcia acromela*), acromelin $C_{17}H_{16}O_8$, m.p. 242°, and acromelidin $C_{17}H_{20}O_9$, m.p. 162° (H. 1907). *T. flavicans*, var. *cinerascens*, physcion and acromelin (H. 1907)

Umbilicaria pustulata (*Gyrophora pustulata*), gyrophoric acid ($C_{18}H_{18}O_7$ (?) (Stenhouse, Annalen, 70, 218; Z. 1898; H. 1898).

Urceolaria lichens, collected from the basalt rock of the Vogelsberg in Upper Hessia, contain lecanoric and erythric acids (Schunck, Mem. Chem. Soc. 1, 71).

Urceolaria scruposa, var. *vulgaris*, atranorin and lecanoric acid (H. 1898, 1904, 1907); patellaric acid (Z. 1902). *U. cretacea* (*U. scruposa*, var. *gypsacea*), lecanoric acid, and palettaric acid (H. 1898, 1911; *cp.* Zopf, 1897).

Usnea barbata (*Lichen barbatus, Parmelia barbata*), usnic acid (Rochleder and Heldt, Annalen, 48, 8; Stenhouse, *ibid.* 155, 51) and lichenin (Berzelius, Scherer's **Annalen, 3, 205;**

Hesse, Annalen, 137, 241; Ber. 10, 1324), usnic and barbatic acids (H. 1898); emulsin (Hérissey, J. Pharm. Chim. [vi.] 7, 577). *U. barbata* f. *dasypoga*, usnic acid and usnaric acid $C_{30}H_{22}O_{15}$, m.p. 240°–260° (H. 1898), *d*-usnic, usnaric, and alectoric acids (H. 1900); barbatic, usnic, and usnaric acids, but no alectoric acid (Z. 1902); alectoric acid (H. 1903). *U. barbata*, var. *ceratina*, usnic acid $C_{18}H_{16}O_7$, m.p. 195°–196°, and barbatin (H. Annalen, 1895, 284, 157). *U. barbata α-florida*, *d*-usnic, usnaric, and parellic acids, and usnarin (H. 1902). *U. ceratina*, usnic acid, barbatic acid and barbatin (H. 1898). *U. ceratina* (Black Forest), barbatic and usnic acids (Z. 1902), *d*-usnic acid, barbatic acid, and barbatin (H. 1903) (Java cinchona bark), *d*-usnic, usnaric, and parellic acids and ceratin (H. 1903). *U. ceratina β-hirta*, Bolivian, *d*-usnic, usnaric, plicatic, and barbatic acids (H. 1903). *U. barbata* (*β*-) *hirta*, *d*-usnic, usnaric, and barbatic acids, and usnarin (H. 1902), atranorin (H. 1906). *U. barbata* (*β*-) *hirta*, (St. Thomas), *d*-usnic and usnaric acids, and santhomic acid $C_{11}H_{14}O_4$, m.p. 166° (H. 1902). *U. hirta*, usnic acid (Knop, Annalen, 49, 103), usnic acid, alectoric acid, hirtic acid, m.p. 98°, and hirtellic acid (m.p. 215° decomp.) (Z. 1903). *U. cernuta*, *d*-usnic and usnaric acids (Z. 1902). *U. longissima*, barbatic and usnic acids (Z. 1897; H. 1898). *U. longissima* (from Amani), ramalic acid, *d*-usnic acid, and dirhizonic acid $C_{18}H_{16}O_5(OMe)_2$, m.p. 189° (H. 1906). *U. florida*, usnic acid (Knop, Annalen, 49, 103); usnic acid and hirtellic acid (Z. 1904). *U. schraderi*, *d*-usnic acid and usnaric acid (Z. 1905). *U. microcarpa*, *d*-usnic acid and usnaric acid (Z. 1905). *U. articulata*, var. *intestiniformis* (Indian cinchona bark), *d*-usnic acid, barbatic acid, and articulatic acid $C_{18}H_{16}O_{10}$ (?) (H. 1907). *U. plicata*, *d*-usnic acid, usnaric acid, usnarin, and plicatic acid $C_{20}H_{33}O_8(OMe)$, m.p. 133° (H. 1900). *U. scruposa*, atranorin and lecanoric acid (Z. 1902).

Pertusaria dealbata, Nyl. (*Variolaria dealbata*, *Lichen dealbatus*), variolarin (Robiquet, Annalen, 42, 236; 58, 320). Schunck found crustaceous *Variolaria* collected on the basalt rocks of the Vogelsberg in Upper Hessia, to contain lecanoric and erythric acids.

Xanthoria parietina (*Parmelia parietina*, *Physcia parietina*), atranorin and physcion (H. 1898, *X. lychnea*, physcion (H. 1898). *X. candelaria* (*X. controversa*, *X. lychnea*, var. *pygmæa*, *X. parietina*, var. *lychnea*), parietin, m.p. 202° (Z. 1904). A. G. P.

LICKNER'S BLUE. A silicate of cobalt and potassium. A variety of smalt; *v.* Cobalt.

LIDDITE *v.* Explosives.

LIEBERMANN and **KOSTANECKI'S RULE** *v.* Colour and Chemical constitution.

LIEBERMANN'S REACTION *v.* Phenol and its homologues.

LIEBIGITE. Hydrated carbonate of uranium and calcium occurring as a thin green coating on pitchblende (of which it is an alteration product) from Adrianople in Turkey, Joachimsthal in Bohemia, and Johanngeorgenstadt and Schneeberg in Saxony. A determination of the optical characters of the minute crystals (E. S. Larsen, 1917) suggests the identity of liebigite with uranothallite of which the formula is $Ca_2U(CO_3)_4{\cdot}10H_2O$. L. J. S.

LIÈGE BLACK. *Blue black v.* Pigments

LIEN, LIENADEN *v.* Synthetic drugs.

LIEVRITE *v.* Ilvaite.

LIGHT CARBURETTED HYDROGEN. *Marsh gas v.* Methyl.

LIGNIN (**LIGNOSE**) $C_{27}H_{31}O_9$ or $C_{40}H_{45}O_{13}$ (Paschke) ($C_{40}H_{46}O_{15}$, Beckmann) may be prepared from straw by treatment with alkali carbonate, precipitation from the extract with acid, and purified by repeated solution in alkali and reprecipitation with acid (Paschke, Zeitsch. angew. Chem. 1921, 34, 465). A constituent of woody substance, jute, acrogens, &c. The colour reaction produced when wood is treated with phloroglucinol, *p*-nitroaniline, &c., is not due to lignin, but to aldehydes, mainly coniferaldehyde, accompanying the lignin (Crocker, J. Ind. Eng. Chem. 1921, 13, 625).

Lignin heated with ten or twelve times its weight of potassium hydroxide for 40 minutes at 280° gives a 20 p.c. yield of oxalic acid.

LIGNIN DYNAMITE *v.* Explosives.

LIGNITE *v.* Fuel.

LIGNOCERIC ACID $C_{23}H_{47}COOH$. A white crystalline solid, m.p. 80·5°, found in the solid paraffin obtained from beechwood tar (Hell and Hermanns, Ber. 1880, 1713) and in earth nut oil (Kreiling, *ibid.* 1888, 880). Found among the products of the dry distillation of oak-bark. Soluble in alcohol. Forms a lithium salt sparingly soluble in methyl alcohol by means of which it may be purified.

LIGNUM COLUBRINUM *v.* Nux vomica.

LIMA WOOD. A variety of Brazil wood (*q.v.*).

LIME *v.* Calcium; also Cements.

LIME, BISULPHITE OF, *v* Calcium.

LIME BURNING *v.* Calcium.

LIME, HYDRAULIC, *v.* Cements.

LIME JUICE. Analyses of lime juice made by Huerre (J. Pharm. Chim. 1919, 20, 5) yielded: sp.gr. 1·052–1·064; citric acid, 7·0–7·5; malic acid, 0·50–0·60; tartaric acid, 0; sucrose, 0·40–0·50; invert sugar, 1·8–2·0; pectins, &c., 0·40: ash, 1·6–1·8 per 100 c.c., *v.* Citric acid.

LIME-OIL *v.* Oils, Essential.

LIME, SUPERPHOSPHATE OF, *v.* Calcium; also Fertilisers.

LIMESTONE (*Kalkstein*, Ger.; *Calcaire*, Fr.). A rock composed essentially of calcium carbonate ($CaCO_3$) in the form of the mineral calcite. Owing, however, to the frequent presence of mechanically admixed impurities and to variations in texture, the rocks of this class exhibit wide differences in character (*v.* Marble, Chalk, Lithographic stone, Marl, Travertine). A snow-white crystalline limestone—*i.e.* a statuary marble—is quite compact, and is pure calcium carbonate, consisting, in fact, of a granular aggregate of calcite crystals. With the admixture of clayey material there may be a gradual passage through argillaceous limestone to calcareous mudstone or to an incoherent marl. Other limestones, containing mechanically admixed impurities of various kinds, are described as siliceous, sandy, carbonaceous, bituminous, ferruginous, and phosphatic limestones. In dolomitic or magnesian limestones, dolomite is present in addition to calcite. Sp.gr. 2·6–2·8 for the denser non-porous varieties; crushing strength, 200–800 tons per square foot. The following analyses are of: I, Bluish-grey, compact crystalline limestone of Carboniferous age from Horton quarries, Settle, Yorkshire; also P_2O_5, 0·17, MnO trace. II, Carboniferous Limestone ('Hopton Wood stone') from Hopton Wood quarries, Middleton, Derbyshire. III, Dark-cream, coarse-grained, granular limestone ('Mill-grit weatherstone'), *Inferior Oolite, from Leckhampton* quarries, Cheltenham, Gloucestershire; also FeO 0·26, K_2O+Na_2O 0·29. IV, Cream-coloured, coarse-grained, granular limestone, Great Oolite, from Box Ground quarries, Bath, Wiltshire. V, Light dove-coloured, fine-grained, granular limestone from Portland, Dorsetshire. VI, Yellowish-brown siliceous limestone, Upper Oolite, from Chilmark quarries, Tisbury, Wiltshire.

	I.	II	III	IV.	V	VI.
CaO .	54·70	55·38	55·04	52·93	53·69	44·2
MgO .	0·15	0·22	0·51	1·19	0·65	1·8
Al_2O_3	0·05	—	0·51	1·20	0·27	2·0
Fe_2O_3 .	[illegible]	0·25	0·23			
CO_2 .	43·03	43·75	40·11	42·90	42·00	36·7
SiO_2 .	0·96	0·75	0·91	-	3·19	10·4
SO_3 .	0·18	—	—	—	0·10	—
H_2O, &c.	0·30	0·10	3·07	1·78	0·10	4·2
	99·75	100·45	100·96	100·00	100·00	99·3
Sp.gr. .	2·72	2·54	2·33	2·07	2·20	2·48
$CaCO_3$.	97·45	98·90	98·25	94·52	95·75	79·0

The majority of limestones are bedded rocks of sedimentary origin, and are composed of the calcareous remains of marine organisms. As a general rule the compactness of a limestone is a measure of its geological age; the harder and more compact varieties belonging to the Silurian and Carboniferous Systems, whilst those of the Jurassic, Cretaceous, and Eocene Systems are less coherent. Limestones may also be formed by the direct precipitation of calcium carbonate from calcareous waters or springs, *e.g.* travertine (*q.v.*) and stalagmitic marble (*v.* MARBLE). Although limestones often resemble some other kinds of rocks in their appearance, they can always readily be recognised by the fact that they easily yield to the knife and effervesce with cold dilute acid (those containing much magnesium effervesce only with hot acid). In addition to their extensive application as building stones, road-metal, &c., limestones are much used for making lime and in the manufacture of mortars and cements of various kinds (*v.* CEMENTS); in the manufacture of soda, carbon dioxide, &c.; as fluxes in smelting; as a polishing material; and as fertilisers, either in the powdered form or burnt as lime. Limestone rocks are also of importance as the depositories of ores of various kinds. Iron-ores and zinc-ores, as well as phosphates, frequently occur as metasomatic replacements of limestone; and veins of lead-ore and fluor-spar are usually richer where they intersect limestones.

References.—G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903; A. Harker, Petrology for Students, 5th ed., 1919; for British Limestones *v.* J. A. Howe, Geology of Building Stones, 1910. On economic questions much has been written in the geological survey publications of the United States. L. J. S.

LIMESTONE, MAGNESIAN, *v.* CALCIUM, MAGNESIUM, and DOLOMITE

LIMNITE. A hydrated ferric oxide

$Fe_2O_3·3H_2O$ or $Fe(OH)_3$

containing Fe_2O_3 74·7, Fe 52·3 p.c., and corresponding with gibbsite $Al_2O_3·3H_2O$. Whilst, however, gibbsite (*q.v.*) occurs as a definitely crystallised mineral, the existence of limnite is somewhat doubtful. Very few analyses show the presence of a sufficient quantity of water *(25·3 p.c.) to satisfy the above formula. Further,* since limnite does not differ from some kinds of limonite in its external characters (earthy or ochreous, with brownish-yellow streak), the material has been regarded as being colloidal limonite with extra adsorbed water. The name limnite, from *λίμνη*, a bog, has practically the same meaning, so far as regards its derivation, as the name limonite (*q.v.*); and it includes also some bog-iron-ores. The mineral was originally described by R. Hermann in 1842 under the name *Quellerz* from bogs in govt. Nizhni-Novgorod. L. J. S.

LIMOGES ENAMELS *v.* ENAMELS.

LIMONITE or **Brown Iron-Ore.** A hydrated ferric oxide $2Fe_2O_3,3H_2O$ of importance as an ore of iron (Fe_2O_3, 85·5; Fe, 59·9 p.c.). It is not found as crystals,[1] but often occurs as rounded, stalactitic, or mamillated forms with an internal radially fibrous (crystalline) structure. This fibrous material when examined in polarised light is found to possess quite definite optical characters. The surface of such masses is sometimes black and lustrous with a pitchy appearance (German, 'Glaskopf'), but here, as in all other instances, the streak of the mineral is of a very characteristic brownish yellow colour. Concretionary (pisolitic) and earthy or ochreous masses are also of common occurrence. Material of this kind is colloidal in character and contains a variable amount of water, grading on one side into xanthosiderite ($Fe_2O_3,2H_2O$) and limnite ($Fe_2O_3·3H_2O$) (*q.v.*). A. Lacroix (1901) and F. Cornu (1909) have suggested that the term 'stilpnosiderite' be applied to the colloidal forms and limonite restricted to the crystalline. The sp.gr. varies from 3·6 to 4·0, reaching the higher value in the compact, fibrous material. Limonite is of abundant occurrence in nature as the final product of weathering of all iron-bearing minerals. Pseudomorphs of limonite after crystals of iron-pyrites and other minerals are well known; and the 'iron hat' or 'gossan' of mineral-lodes consists mainly of limonite. As an earthy ochreous deposit it separates from the waters of chalybeate springs, and in peat-bogs and at the bottom of pools and lakes. Such deposits are known as bog-iron-ore (*q.v.*), lake-ore, &c., and the name limonite (from *λειμών*, a meadow) means, in fact, meadow-ore. The phosphates they contain are of organic origin. The brown iron-ores extensively mined in Northamptonshire, the north of Spain, Luxembourg and Lorraine (here an oolitic ore known as 'minette'), and many other places, occur as beds in sedimentary rocks. Ochreous limonite is used for making paint, for colouring and glazing tiles, and in the manufacture of linoleum, brown paper, &c. Bog-iron-ore has been used in gas purifiers, and for extracting the sulphur from waste sulphurous gases. L. J. S.

LINADIN *v.* SYNTHETIC DRUGS.

LINAMARIN *v.* GLUCOSIDES.

LINARIN. A glucoside found in the flowers and leaves of *Linaria vulgaris* (Mill.) (Klobb, Compt. rend. 1907, 145, 331).

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[1] The only hydroxide of iron that occurs as definite crystals is goethite, $Fe_2O_3·H_2O$ (*q.v.*).

LINNÆITE. A sulphide of cobalt, Co_3S_4 or $CoO{\cdot}Co_2S_3$, crystallised in the cubic system and analogous to spinel. The cobalt (11–45 p.c.) is usually largely replaced by nickel (0–42 p.c.), iron (2–5 p.c.), and copper (0–4 p.c.). The nickel-rich variety is known as *siegenite*, from Siegen in Westphalia. It is often found as bright octahedra of a steel-grey colour tarnishing to copper-red; also as compact granular masses, and as grains. Brittle; H. 5½; sp.gr. 4·8–5·0; soluble in nitric acid with separation of sulphur. It is found with other metalliferous ores at Bastnas in Sweden, Musen near Siegen in Westphalia, Madison Co. in Missouri, Mineral Hill in Maryland, at Santa Fé mine in the state of Chiapas in Mexico. At the last-named locality the mineral carries 0·53 p.c. of gold. L. J. S.

LINOLENIC ACID. Linolenic acid $C_{18}H_{30}O_2$ is a characteristic constituent of drying oils, notably linseed oil, and also occurs in certain animal fats, such as horse fat. It is a colourless oily liquid which rapidly absorbs oxygen from the air and turns brown Sp gr. at 15°, 0·9228 (Hehner and Mitchell); b p. under pressure of 0 mm., 157°–158° (Bedford) It combines with bromine to form a white hexabromide (m p. 179°–180°), which when reduced with nascent hydrogen yields linolenic acid. When oxidised with alkaline potassium permanganate it yields, as the principal product, hexahydroxystearic acid (linusic acid), m p. 204°–205°. The existence of an isomeride of linolenic acid, iso*linolenic acid*, was inferred by Hazura from the fact that the liquid fatty acids of linseed oil also yielded an oxidation product (iso*linusic acid*), m.p 173°–175°; but Bedford's experiments tend to show that Hazura's *iso*linusic acid is sativic acid, the main oxidation product of linolic acid, which has the same melting-point. Bedford concludes that when the insoluble hexabromide obtained by brominating linseed oil fatty acids is reduced by means of zinc and alcoholic hydrochloric acid it yields a mixture of two isomeric acids, *a*- and *β*-linolenic acids, the former again yielding the hexabromide on bromination, whilst the latter absorbs four atoms of bromine and yields a liquid tetrabromide $C_{18}H_{30}Br_4O_2$, mistaken by Hazura for *iso*linolenic hexabromide.

Linolenic acid may be quantitatively reduced to stearic acid by hydrogenation in presence of a metallic catalyst. The ethyl ester of linolenic acid boils at 132°–133° at a pressure of 0·001 mm., $n_D^{20}=1{\cdot}46753$. C. A. M.

LINOLIC ACID. Linolic acid $C_{18}H_{32}O_2$ is present as a glyceride in many vegetable oils, and can be separated in large amount from non-drying oils such as maize and cotton-seed oils. It is a pale yellow liquid which remains fluid at −18°. Sp.gr. at 14°, 0·9206. It differs from oleic acid in not yielding a solid compound when treated with nitrous acid (elaidin reaction). It absorbs oxygen rapidly from the air, and combines with bromine to form a tetrabromide $C_{18}H_{32}O_2Br_4$ (m.p. 114°–115°), which is readily soluble in ether, alcohol, and benzene, but sparingly soluble in petroleum spirit. When reduced with nascent hydrogen it yields linolic acid, whilst when oxidised with alkaline potassium permanganate, it yields as its main oxidation product, tetrahydroxystearic acid (sativic acid). According to Bedford there are two isomeric linolic acids, which he terms *a*- and *β*-linolic acid, the former yielding the solid tetrabromide (m.p. 114°–115°), and the latter a liquid bromide. Tariric acid, telfairic acid, and elæostearic acid (tung oil) are isomerides of linolic acid. C. A. M.

LINOXYN. The tough elastic product of the oxidisation of linseed oil.

LINSEED. The seeds of *Linum usitatissimum* (Linn.). There are two chief varieties, with white and blue flowers respectively. The plant requires moist heat, but is not suited to great heat and drought or to frosty conditions. It therefore does best on the seacoast or plains and hills where the rainfall is abundant or dews and fogs frequent, and in damp soils rather than in dry ones. It is grown in many countries, but the chief sources of the linseed of commerce are Russia and India.

The average composition, as given by König, as the mean of 61 analyses, is—

Water	Protein	Fat	Nitrogen-free substances	Crude fibre	Ash
9 0	22·8	34·4	22·8	6 8	4·2

All the constituents are liable to considerable variation, *e g.* protein 16–31 p.c., fat 22–40 p.c. The 'protein' of linseed is almost wholly albuminoid in nature, not more than 2–4 p.c. of it being in other forms (a small portion as a glucoside). Linseed contains a characteristic mucilage (about 6 p.c. of its weight), which exists mainly in the membranes of the outer cells and causes the seeds when macerated with water to swell up so much as to burst the cell-walls. When linseed is boiled with water, the mixture thickens owing to the solution of this mucilage.

Linseed is very largely consumed, being used as a food for young calves (as a partial substitute for milk), and in enormous quantities in the preparation of linseed oil, so important in the preparation of varnishes, paints, and linoleum, the by-product linseed cake or linseed meal, also forming an important cattle food, valuable not only for its nutritive value, but also on account of its richness in the manurial substances, nitrogen, phosphoric acid, and potash.

The ash of linseed contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
30·2	2·1	8 1	14·3	1·1	40·5	2·3	1·2	0·2

Of pure linseed cakes there are two types, viz. those from which the oil has been *expressed*, and those from which the oil has been *extracted* by the use of volatile solvents; the former are richer in fat and more digestible, the latter richer in albuminoids and ash. The following average compositions are given by Kellner:—

	Water	Protein	Fat	*N*-free extract	Crude fibre	Ash
Expressed cake	11·0	33·5	8·6	31·7	8·7	6·5
Extracted ,,	10·2	37·4	3·8	32·7	9·1	6·8

It was shown by Jorissen (Bull. Acad. Roy. Belg. 1883, 3, 5, 750) that linseed contains a cyanogenetic glucoside. This glucoside, named *linamarin* by Jorissen, has been shown to be identical with *phaseolunatin* (*a*-dextrose ether of acetone cyanohydrin) which occurs in the beans of *Phaseolus lunatus* (Linn.) (Dunstan, Auld and Henry, Proc. Roy. Soc. 1906, B. 78, 145). This substance is present in young linseed plants, in linseed, and also in linseed cake. In the latter, to the extent of yielding 0·03 to 0·04 p.c. of hydrocyanic acid, but the enzyme which hydrolyses the glucoside, and which is present in the seed, is destroyed by the high temperature employed in expressing the oil, and is therefore absent from the cake (*Dunstan and Auld, J. Soc. Chem. Ind.* 1908, 428). *Pure linseed cake is therefore not likely* to act as a poison, but *might* do so if prepared by cold pressure, or if fed along with any foodstuff containing the enzyme necessary for the hydrolysis of the glucoside. Linseed grown in hot, dry climates contains more hydrocyanic acid and more active hydrolysing enzyme than when grown under cool, damp conditions (Collins and Blair, Chem. News, 1915, 19).

H. I.

LINSEED GUM *v.* GUM.

LINSEED OIL, flax seed oil, is obtained from the seeds of the flax plant, *Linum usitatissimum* (Linn.), a native of Central Asia. The principal countries where it is grown in considerable quantities to yield oil seed are the Argentine, India, the United States, Canada, and Russia. Notable quantities of seed are also produced in Morocco. The seed is also cultivated in Australia and in S. Africa.

Two qualities of Russian seed are recognised in the trade, known, according to their source, as Baltic and Black Sea seed, hence the terms 'Baltic linseed oil' and 'Black Sea linseed oil.' The oil expressed from Indian seed is known as 'East India oil.' The Baltic linseed yields the best drying oil; this is explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed 5 p.c. (and more) of hemp seed and (or) ravison seed are usually present. Indian seed is frequently mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. It has been proved that when the Indian linseed is carefully separated from the foreign seeds and then expressed, the oil possesses as good drying properties as does best Russian oil. During latter years, more attention having been paid in India to this growing industry, the quality of seed has improved. Argentine seed, yielding the (River) Plate oil (La Plata oil), being badly harvested, contains much chaff and admixed fibres; if more care were exercised, La Plata oil also would more regularly approach Baltic oil in drying properties. The United States, which, until a few years ago, had been importing East Indian seed, have so considerably increased the home production that they rank occasionally (*i.e.* when the harvest is plentiful) amongst the exporting countries. Canada also is exporting considerable quantities of linseed.

The proportion of linseed oil in the seed varies with the origin of the seed and also with the seasons. It may be accepted that linseed contains from 32 to 42 p.c. of oil, according to the origin. On a large scale the quantity of linseed oil obtained from good seed does not exceed 35 p.c.

The variations in the oil expressed from linseed of different origin are shown in the following results obtained by Sheppard (J. Ind. Eng. Chem. 1912, 4, 14):—

Seed	Oil	Sp.gr. at 15°	Av. weight per seed	Oleaginous impurities	Non-oleaginous impurities	Oil in total impurities
	p.c.		mg.	p.c	p c.	p.c.
1 American	39·67	1·1413	4·61	1·5	1·69	10·1
2 ,,	39 40	—	4·53	1·01	1·05	—
3 La Plata	36·98	1·1415	5·56	0·58	5·64	14·1
4 Calcutta.	40·82	1·1326	5·41	4·85	5 03	14·9
5 Bombay.	41·23	1·1182	7·88	0·81	2·80	—
6 S. Russia	39·11	1·1375	5·74	5·05	1·71	—
7 N. Russia	36 95	1·1458	4·19	3·31	1·97	—

The dark colour of La Plata oil is attributable to the non-oleaginous impurities.

On cold-pressing, a golden yellow coloured oil is obtained, having a pleasant taste, so that it can be used as an edible oil. Considerable quantities are being expressed for this purpose in Russia, Hungary, Germany, and India. In some parts of Germany the oil is used either as such, or (as 'Leinoelschmalz') in admixture with tallow or (and) lard for edible purposes. By far the largest quantities of oil are, however, employed in the arts. In that case the seed is crushed between rollers and then heated to about 160°F. in the mixing kettle; subsequently the seed is expressed while still warm. The oil so obtained has a yellowish-brown hue, and is somewhat turbid, owing to traces of moisture and mucilaginous matter. The press cakes retain about 10 p.c. of oil; they are used as one of the most valuable and wholesome cattle foods.

On storing the oil, the moisture and the mucilaginous matter gradually settle out, and the oil hereby acquires a higher value, especially for some technical uses, as in the making of varnish. Such oil, sometimes kept for years, is known as 'tanked oil.' The suitability for varnish-making purposes is ascertained by heating rapidly the linseed oil in a test tube. Oil from which gelatinous matter separates is considered unsuitable. Seed pressed in a comparatively fresh ('green') state yields oil containing larger quantities of 'mucilage' than seed three to six months old. The gelatinous matter ('mucilage' or 'spawn' or 'break') contains phosphates and traces of sulphates.

The bulk of linseed oil is at present produced by expression. The main reason for this is that the hot-pressed cake is valuable as cattle food, whilst linseed meal obtained by extraction with solvents could only be used as manure, at any rate in this country. Occasionally linseed has been extracted with solvents, as it was thought that the oil so obtained, being richer in unsaturated acids, and containing less of the mucilaginous matter, would be more suitable for the paint and varnish trades. This has, however, not been borne out in practice, extracted oil having been found unsuitable as a paint oil. Moreover, the oil obtained by extracting with carbon disulphide, petroleum spirit, &c., possesses an inferior colour and a more unpleasant smell than expressed oil. Therefore it would only be profitable to extract damaged seed, which would be unsuitable for cattle food.

A rapid method for removing the impurities in the crude oil is to refine it, which is done on a large scale by treating crude linseed oil with 1–2 p.c. of a somewhat concentrated sulphuric acid. The charred mass carries down with it the bulk of impurities contained in the crude oil. For the manufacture of the best and finest kinds of linseed oil ('artists' oil'), the refined oil is subjected to 'sun-bleaching,' by exposure in shallow zinc trays under glass to the action of sunlight. Powdered lead placed in the trays accelerates the bleaching process. A method of bleaching linseed oil by exposure to the Cooper-Hewitt mercury lamp has also been introduced. Dark linseed oils intended for soft soap are usually bleached in the soap works by treatment with a small amount of caustic potash. The soap which is formed carries down with it the colouring matters.

The chemical composition of linseed oil is not yet fully known It may, however, be stated broadly that linseed oil contains about 10 p.c. of solid fatty acids, amongst which palmitic acid, stearic acid, and arachidic acid have been identified. In addition thereto, the oil contains a high proportion of linolenic acid and linolic acid. The proportion of oleic acid, which Hazura gave as amounting to about 5 p.c., may possibly, according to later statements, have to be raised to 15 p.c. The 'isolinolenic acid,' which Hazura stated to occur in linseed oil has not been definitely proved to be a chemical individual. Rollett (Zeitsch. physiol Chem. 1909, 72, 422) doubts the existence of a β-linolenic acid, which Erdmann and Bedford state is obtainable from linolenic acid (Ber. 1909, 41, 1324; Zeitsch. physiol Chem. 1910, 79, 76) On the whole, the balance of evidence supports the view of Erdmann and Bedford.

Several mixed glycerides have been identified in linseed oil. Thus Schicht (Seifenfabr. 1914, 34, 673) separated linolopalmitostearin by chilling a solution of linseed oil in petroleum spirit, alcohol and ether, whilst the mother liquor contained other compounds which, judging by their chemical characters, were probably dioleostearin and linolodistearin. The insoluble bromide yielded by linseed oil is also probably produced by a mixed glyceride in the oil.

Linseed oil has a higher specific gravity than any fatty oil that would be used to adulterate it, with the exception of tung oil. Hence, in the trade a specific gravity lower than 0·93 is considered to indicate adulteration with other fatty oils or mineral oils.

The higher the specific gravity of a linseed oil, the more suitable it is for the purposes of the paint and varnish manufacturer. The value of the oil for this purpose is also expressed in a general way by the magnitude of the iodine value. Linseed oil has, with the exception of perilla oil, the highest value of all known fatty oils. Hence the iodine test is of value for identifying a sample. The iodine value of linseed oil should not fall below 170 (La Plata and North American oils), although much higher iodine values reaching as high a figure as 205 have been recorded. Thus Indian oils usually absorb from 183 to 192 p.c., and Baltic oil from 190 to 200 p.c.

Linseed oil is characterised by giving a high proportion of a bromide insoluble in ether, apparently the bromide of a mixed glyceride (Hehner and Mitchell, Analyst, 1898, 23, 315) A more accurate modification of the test has been devised by Davidson (J. Ind. Eng. Chem. 1921, 13, 801). According to Gemmell (Analyst, 1914, 39, 297) there is a definite relationship between the iodine value of an oil and the amount of insoluble bromide which it yields.

The American Society for Testing Materials has issued the following specifications for raw linseed oil from N. American seed: Sp.gr. at 15·5°, 0·936 to 0·932; at 25°, 0·931 to 0·927; acid value, 6·0 (max.); saponification value, 195 to 189; unsaponifiable matter, 1·50 p.c. (max.); refractive index at 25°, 1·4805 to 1·4790; and iodine value (Hanüs), 178 (min.). All tests must be applied to the oil filtered through paper, at 15·5° to 26·7°, immediately before weighing. (*Cf.* Davidson, J. Ind. Eng. Chem. 1921, 13, 801; in abstr., J. Soc. Chem. Ind. 1921, 817 A.)

When the price of linseed oil is high adulteration is practised to a very considerable extent. For the methods devised for detecting these adulterants the reader is referred to Lewkowitsch's Chemical Technology.

Linseed oil (provided its price is not excessively high) is very extensively used as stock material for soft soaps; for this purpose those oils are especially employed which have a comparatively low iodine value. The presence of mucilage is not objectionable in the case of oils for soap-making

A further important application of linseed oil is found in the manufacture of boiled oil for paints, varnishes, lithographic varnishes, and for the manufacture of linoleum. No other drying oil approaches the properties of linseed oil, the drying oil *par excellence*. Hence linseed oil is also the best oil for making putty. Linseed oil is further largely used in the preparation of plastic masses.

Boiled oil is obtained by heating linseed oil with driers to a temperature of about 150°C. The process is carried out by introducing the oil into a cylindrical vessel provided with a heating coil and agitating gear, so as to produce an intimate intermixture between oil and drier while they are heated to the desired temperature.

According to the quality and the amount of drier added, and the length of time during which the oil is heated ('boiled'), pale or dark oils are produced. The former are known in commerce as 'pale boiled oils,' the latter as 'double boiled oils.' The temperature of 'boiling' can be reduced even to 120°C. when 'liquid driers' (solutions of lead linoleate, &c., in linseed oil) are used. They are merely dissolved in the oil and the operation is assisted, if required, by a current of air.

This last process yields somewhat inferior drying oils to those obtained by boiling at 150°C. with lead oxide, &c. It has, however, been inferred therefrom that in order to obtain a quickly drying oil it suffices to prepare a solution of metallic salts in oil. This view has even led to the preparation of 'boiled oils' in the cold, by merely adding to linseed oil a solution of lead linoleate or manganese linoleate, and carefully mixing it with the oil. (An oil having the properties of a 'boiled' oil can also be prepared by carefully grinding linseed oil with manganese borate in the cold.) These 'boiled oils' are, therefore, identical with the product which painters used to prepare themselves from raw linseed oil by grinding it with a drier. Such oils naturally do not dry so rapidly as do the oils prepared at a higher temperature; they behave more nearly like raw linseed oil as regards the time required to 'dry.' The investigations of Holden and Radcliffe (J. Soc. Dyers and Colourists, 1918, **34**, 134) have shown that the rate of drying of linseed oil increases with the temperature, but that the higher the temperature the lower the maximum increase in weight, and the less the influence of added driers. For example, when dried just below 34° linseed oil gains 17 to 18 p.c. in weight, whereas at 100° the maximum increase is much less (7 to 8 p.c.), and at 150° there is no increase in weight, probably owing to the evolution of volatile products. The greater durability of linseed oil films dried at high temperatures must be attributed to the more rapid volatilisation of non-drying constituents. The volatile products of linseed oil oxidised at 100° contain aldehydes (acrolein) and traces of oil.

These results are in accordance with the conclusions of Salway (J. Chem. Soc. 1916, 109, 138), that in the drying of linseed oil oxygenides are first formed, and these tend to form dioxygenides, which would decompose with the formation of a mixture of aldehydes (including acrolein), and carbon monoxide and dioxide, formic, acetic, and acrylic acids. For the factors affecting the oxygen absorption of linseed oil see Waelle, J. Soc. Chem. Ind. 1920, 39, 48 T; Coffey, Chem. Soc. Trans. 1921, 1152. Manganese salts are much more effective than lead salts as driers, whilst cerium linoleate is more active than lead linoleate, but is inferior to manganese and cobalt linoleates (Morrell, J. Chem. Soc. 1918, 113, 111).

The conclusions of Ingle (J. Soc. Chem. Ind. 1917, 36, 319) on the course of the chemical reactions involved in the drying of lead linolenate are supported by the experiments of Morrell (*loc. cit.*) upon the cerium salts prepared from drying oils. When drying oils are heated there appears to be a change in the intramolecular linkings prior to polymerisation.

Experiments by Friend (J. Chem. Soc. 1917, 111, 162) have shown that linseed oil contracts on oxidation. The density of the oil increases as the absorption of oxygen proceeds, whilst the volume first increases and then gradually decreases.

With regard to the employment of other oils in the manufacture of boiled oils and the adulterants of boiled oils, *cp.* Lewkowitsch, Chemical Technology.

Linseed oil is also used in the manufacture of 'vulcanised oils,' and for extracting indiarubber from 'waste rubber' By heating linseed oil with sulphur, the official *oleum lini sulf.* is prepared.

Owing to the high price of linseed oil during the last few years mixtures of tung oil, menhaden oil, and soya bean oil have been used as substitutes for it in paints and varnishes, special drying agents being used to accelerate the drying properties of the mixtures.

A method of preparing a substitute for boiled linseed oil by blowing superheated steam through fish oils previously heated at 235° to 240° is described in Ger. Pat. 272,465 of 1910. The drying properties are stated to be superior to that of linseed oil. J. L.

LINTONITE *v.* THOMSONITE.

LIPASE, the enzyme which hydrolyses fats to glycerol and fatty acids, is of considerable importance in animal physiology and in germinating seeds. It is used industrially in the manufacture of glycerol and fatty acids, and is concerned in the phenomenon of rancidity. The knowledge of it, however, is still in a somewhat fragmentary state. It was first discovered by Reynolds Green (Proc. Roy. Soc. 1890, 48, 370) in the germinating seed of *Ricinus communis* (Linn.), and has since been found in many other seeds, usually in the germinating rather than in the resting stage; it also occurs in mould fungi and in yeast. Lipoclastic enzymes are present in most animal tissues, the liver being the most active. The enzyme appears to cling to the solid particles of tissue cells.

Vegetable lipase is very sparingly soluble in water, and it is doubtful whether active filtered extracts of the enzyme can be obtained. It has been shown by Connstein and others (*see* summary in Asher and Spiro's Ergebnisse der Physiologie, 1904, 3, 194) that *Ricinus* lipase is effective only in the presence of acid, and that it acts preferentially on the natural fats, other ethereal salts being but little attacked by it.

Animal lipase, on the other hand, is quite active in hydrolysing simple esters and acts on the natural fats with difficulty, though this is perhaps due to the difficulty of securing a satisfactory emulsion (*cp* H. E. Armstrong, Proc. Roy. Soc. 1905, 76B, 606, 1906, 78B, 376; Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491).

Commercial pancreatin prepared from the fresh sweetbread of the hog or ox contains a lipase often termed steapsin which acts in an alkaline medium, and is rapidly destroyed by strong alcohol and by all acids except the fatty acids, being the most delicate of the pancreatic enzymes

According to Tanaka (Chem. Soc. Abstr. 1910, i. 800) lipase is present in castor oil seeds in the form of an insoluble zymogen which is readily converted by dilute acid into the insoluble enzyme, the acid acting merely to liberate the enzyme which, when once liberated, is active in a neutral medium. Alternatively, it may be present as a salt which is decomposed by the acid. It is inactive in alkaline solution.

The action of lipase is accelerated by manganese sulphate and by bile salts. All acids are effective in activating the enzyme, action depending on the amount rather than on the concentration of the acid.

Animal lipase may be separated by dialysis, or filtering, into two substances which are inactive singly, but the original activity is restored when they are mixed; the activity of the filtrate is not destroyed by boiling (Magnus, Zeitsch. physiol. Chem. 1904, 42, 149; Rosenheim and Shaw-Mackenzie, J. physiol. 1910, 40). Lipase also exercises synthetic activity (Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491; Hanriot, Compt. rend. 1901, 132, 212).

It is considered by Falk and Sugiura (J. Amer. Chem. Soc. 1915, 37, 217) that castor oil beans contain two enzymes, one soluble in water and more active towards ethyl butyrate, and the other insoluble and more active towards glyceryl triacetate and fats. The former is referred to as esterase and the latter as lipase.

Lipase is also present in soya beans.

Lipase occurs in the fat of fowls in the zymogenic form and becomes active only after death, causing the acidity of the fat to increase (Pennington and Hepburn, J. Amer. Chem. Soc. 1912, 34, 210).

Lipase powder (from Ricinus) loses its activity when kept with neutral fats alone without the presence of either acid or water. Triolein exerted greater action than other fats in this respect.

The ferment process is used for the preparation of soap-stock fatty acids (Connstein, Eng. Pat. 22111, 1902). The ground seeds were made into an emulsion with oils and dilute acetic acid, but the original process was abandoned on account of the losses due to the formation of a middle layer between the fatty and aqueous layers. According to Lewkowitsch (Chemical Technology of Oils, Fats, and Waxes, 1909, 3) it is now customary to prepare a 'ferment' by grinding decorticated castor seeds with a large quantity of water and filtering. The creamy liquor is allowed to ferment spontaneously when a creamy emulsion containing the active enzyme rises to the top. The oil is emulsified by air currents in lead lined vessels with 40 p.c. of water, 5-8 p.c. of the ferment and 0·2 p.c. manganese sulphate, the last substance serving to accelerate the change (Eng. Pat. 25680, 1905). After several days the mixture is warmed to 80°C., and 0·3-0·45 p.c. sulphuric acid (50 p.c.) is added; it is then allowed to settle. Three layers are formed—a bottom aqueous layer containing glycerol, an upper fatty layer and a middle layer consisting of an emulsion, which is allowed to accumulate, and on renewed treatment separates into three layers. The temperature of hydrolysis is maintained above 20°C. and below 42°C.; it should be slightly above the melting-point of a fat. The products so obtained are much lighter in colour than those given by the older processes of hydrolysis.

Tanaka (J. Coll. Eng. Imp. Univ. Tokyo, 1912, 5, 125) has described the preparation of an active lipase from castor oil seeds by digesting the pressed material with a proper amount of acid and then washing to remove all soluble matter. This hydrolyses fats rapidly in the absence of any soluble acid. The shelled seed is crushed in a mortar and the oily mass digested with petroleum spirit for 24 hours, after which the greater part of the oil is removed by squeezing it through calico cloth. The residue is treated twice in the same manner with ether; it is then ground and digested during about 15 minutes with 8 c.c. of N/10 acetic acid to every 10 grams of the meal. The liquid is filtered off and the residue washed several times with water. It is dried in a vacuum desiccator and, when dry, ground fine and sifted through muslin. During washing about 40 p.c. of the material passes into solution. The powder obtained represents about 9 p.c. of the weight of the seeds. It is colourless and tasteless, and may be kept for a long time without undergoing appreciable change (*cf.* Armstrong and Gosney, Proc. Roy. Soc. 1913, B, 86, 586). The enzyme prepared with a weak acid such as acetic is distinctly superior to that obtained when a stronger acid is used.

Prepared as described, if olive oil be digested at 30°C. with about 3–4 p.c. of the powder and from 6-10 times as much water about 90 p.c. of the glyceride is hydrolysed within 7–10 hours.

It is possible to 'overdry' the enzyme when it is required to be used in the absence of water. In such cases the addition of traces of water usually restores the activity. Preparations of the enzyme often vary in activity considerably, a fact which is not surprising when it is remembered that their activity depends on surface condition of the colloid.

The activity of the enzyme is interfered with even by dilute acids, and it is easily rendered inert by excess of acid. Possibly the powder contains an emulsifying constituent on which its activity is largely dependent. Hence it is specially fitted to hydrolyse the oily glycerides of the higher fatty acids and is not suited to act in an aqueous solution. The interaction is inhibited by the products of change, both the fatty acid and glycerol, especially the former.

Under ordinary conditions the hydrolysis of fats by lipase powder is incomplete, and numerous observations are on record to prove that whether of animal or vegetable origin, it can act reversibly. In the case of olive oil and lipase prepared by the Tanaka method, the same equilibrium was attained starting either from the oil in presence of three molecular proportions of water or from the fatty acids and the equivalent of glycerine; the percentage of acid combined being about 38, and the main product a diglyceride indicating that the two primary hydroxyl groups of glycerine are first affected. In presence of more water the rate of both synthetic and hydrolytic changes was decreased, and the equilibrium point established in the direction of greater acidity. Even in presence of 30 molecular proportions of water some synthesis was observed (*cf.* H. E. Armstrong and Gosney, Proc. Roy. Soc. 1914, B, 88, 176).

Rancidity.—The presence of lipase in oily seeds leads to the formation of small quantities of fatty acids, particularly in presence of moisture. Commercial fats of both vegetable and animal origin, if they have not been submitted to a sufficiently high temperature to kill the enzyme during their manufacture, are likely to contain traces of lipase, and this in presence of moisture may cause the formation of free fatty acids. When the fatty acids are further exposed to oxidation, particularly in presence of light, rancidity takes place (*see* further on this point, Lewkowitsch, *l.c.* 1, 35) (*v.* FERMENTATION).

The presence in a fat of other substances on which bacteria can grow increases the probability of rancidity; butter or margarine, for instance, being particularly prone to the change. Fats such as cocoa butter which contain more saturated acids, are less liable to become rancid.

Numerous bacteria exist which split fats anaerobically and oxidise them aerobically, owing to the secretion of lipase. The injurious effect of fat splitting organisms on the quality of dairy products is chiefly due, in addition to their lipoclastic properties, to the production of bitter and odoriferous substances from proteins and casein. The organisms produce lipases which act both in acid and alkaline solution, Sohngen (Proc. K. Acad. Wetensch Amsterdam, 1911, 13, 1200) finds that the decomposition of fat decreases as the amount of acid rises, and that it ceases entirely when the acidity of the culture liquid is about N/50. Mineral acids are more potent than organic acids. It is considered that rancidity can only take place when owing to the action of alkali-producing bacteria and moulds the acidity of dairy products falls below this limit. The decomposition of dairy fats by lipase is favoured by oxygen and light. Lipase is not soluble in ether, fats, or fatty acids.

In commercial palm oil which is prepared in tropical countries under crude conditions, the proportion of fatty acids is considerable and the value of the product much diminished in consequence. Probably much of this development of acid is due to enzyme action. Palm kernels and copra similarly vary greatly in the amount of free acid they contain according to the care taken in their preparation and storage.

E. F. A.

LIPOIODIN. Di-iodobrassidic acid ethyl ester.

LIQUATION. 'When an ore or metallic mixture containing ingredients differing sensibly in fusibility is exposed to a degree of heat sufficient only to melt the most fusible which may flow away from the unmelted mass, this process is termed liquation' (Percy's Metallurgy). In certain cases a mixture of two metals can be roughly separated in this way. For instance, if an alloy of lead and copper be heated to a temperature a little above the melting-point of lead, the lead trickles out, leaving a porous mass behind. The lead contains 2–3 p.c. of copper. The copper contains 25 p.c. of lead. This process is used commercially to separate antimony sulphide from the ore, by heating in earthenware pots with a hole in the bottom, through which the melted sulphide flows.

At the Schemnitz silver works impure lead is purified by melting it on the bed of a furnace, the lower end of which is connected with a large iron pot, heated independently, and into which the lead trickles. Fresh lead is thrown into the furnace from time to time; the melted lead flows into the pot and leaves less fusible alloys behind. The lead in the pot is then made hot, skimmed and poled. The purification of a metal by this means depends upon the formation of less fusible alloys between the metal and the foreign metals present. Pattinson's process (*v.* LEAD) for desilverising lead depends on the formation of such alloys, but in that case the solidified alloys are fished out of the melted lead by a ladle, instead of allowing the lead to flow away from them.

LIQUEFACTION OF GASES. The readiness with which many liquids can be converted into vapours similar in many respects to ordinary gases, suggests the possibility of an intimate relationship between the gaseous and liquid states of matter. Van Helmont, to whom we owe the introduction of the term 'gas,' in the latter part of the 16th century, distinguished between 'gases' and 'vapours,' saying that only the latter could be reduced to the liquid state. Boerhaave (1731) in his Elements of Chemistry (Eng. ed., 249), comments on the impossibility of liquefying air either in the sharpest frost or under pressure. Dalton clearly foresaw the result of subjecting gases to low temperatures and high pressures when he said: 'There can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of whatever kind into liquids; and we ought not to despair of effecting it in low temperatures and by strong pressures exerted upon the unmixed gases.'

The statement in Fourcroy's Chemistry, 2, 74, that Monge and Clouet liquefied sulphur dioxide is one of the earliest recorded references to the liquefaction of a substance commonly recognised as a gas. Shortly afterwards, in 1805–1806, Northmore (Nicholson's Journal, 1805, 12, 368; 1806, 13, 233) succeeded in liquefying chlorine, hydrogen chloride, and sulphur dioxide, by compressing the gases into a strong glass receiver. These results, however, did not attract much attention, and no further work on the liquefaction of gases appeared until 1823.

The discovery of the production of liquid chlorine by heating chlorine hydrate in a closed glass tube, led Faraday to undertake a systematic study of the liquefaction of gases. The method employed in his first series of experiments (Phil. Trans. 1823, 113, 189) was simple. Into the sealed limb of a bent glass tube were placed materials for generating the gas. The other limb of the tube was then sealed and cooled in a freezing mixture of ice and salt. The end containing the reacting substance was heated to generate the gas; the pressure steadily increased as the gas was produced, and ultimately the gas liquefied in the cold limb. In this manner Faraday succeeded in liquefying sulphur dioxide, hydrogen sulphide, 'euchlorine,' cyanogen, ammonia, carbon dioxide, and nitrous oxide, the experiments on the last two gases being often accompanied by violent explosions.

The first experimenter to utilise the evaporation of a liquid under reduced pressure in order to produce low temperatures was Bussy (Ann. Chim. Phys. 1824, 26, 63). By the rapid evaporation of liquid sulphur dioxide he reached temperatures sufficiently low to liquefy chlorine, ammonia, and cyanogen. This method of producing low temperatures soon came into general use.

In 1834 Thilorier (Ann. Chim. Phys. 1835, 60, 427, 432; Annalen, 1839, 30, 122) prepared liquid carbon dioxide on a large scale by what was essentially the method of Faraday, using, however, a wrought iron generator and receiver connected by a copper tube. Moreover, he succeeded in freezing this liquid by allowing it to escape through a jet into a specially constructed drum-shaped box. Solid carbon dioxide has proved of service to subsequent experimenters. A mixture of solid carbon dioxide and ether, often called *Thilorier's mixture*, is even to-day a very valuable refrigerant; by evaporating it under reduced pressure, temperatures as low as −110°C. can be obtained.

In Faraday's second research on the liquefaction of gases (Phil. Trans. 1845, 135, 155) the gases were subjected to the simultaneous influence of high pressure and low temperature. The former was applied by means of two air pumps, and the latter was produced by means of a cooling bath of Thilorier's mixture boiling under diminished pressure. The gases were condensed in suitably shaped tubes of green bottle-glass, the pressures were measured by means of small air gauges inserted in the tubes, and temperatures were recorded by an alcohol thermometer. In these experiments, ethylene, silicon fluoride, phosphine, and boron trifluoride were liquefied, and hydrogen bromide, hydrogen iodide, sulphur dioxide, 'euchlorine,' hydrogen sulphide, ammonia, cyanogen, and nitrous oxide were solidified. Faraday was, however, unable to liquefy hydrogen, nitrogen, oxygen, nitric oxide, or carbon monoxide, although he predicted that, if the temperature could be sufficiently reduced, these gases would pass into the liquid state.

The work of Natterer (J. pr. Chem. 1844, 31, 375; 1845, 35, 169; 1852, 56, 127; Pogg. Ann. 1844, 62, 132; 1855, 94, 436; Wien. Ber. 1850, 5, 351; 1851, 6, 557, 570; 1854, 12, 199), which began in 1844 and extended over several years, placed at the disposal of experimenters a method for obtaining extremely high pressures. Natterer was the first observer to prepare liquid nitrous oxide in quantity. He repeatedly endeavoured to liquefy hydrogen, oxygen, nitrogen, and carbon monoxide, modifying his apparatus from time to time until the gases were subjected to the enormous pressure of 3600 atmospheres. Even the application of Thilorier's mixture to the gases at this pressure failed to effect their liquefaction.

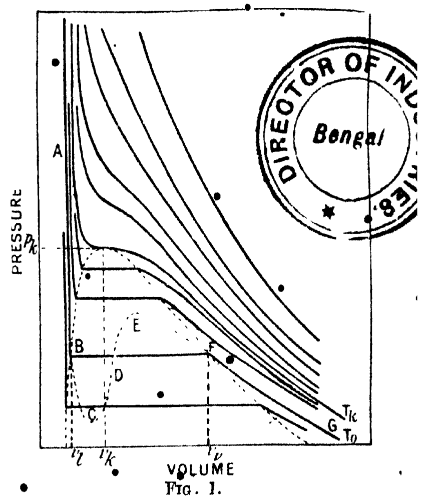
Critical phenomena and the relation between the liquid and gaseous states.—The classical work of Andrews (Phil Trans. 1869, ii. 575; also *ibid.* 1876, ii. 421) marks an era in the development of the subject of the liquefaction of gases. The relative values of temperature and pressure in effecting liquefaction had, up to that date, not been understood. As early as 1822, Cagniard de la Tour (Ann. Chim. Phys. 1822, 21, 127; 1823, 22, 411) had performed a series of experiments on heating volatile liquids in closed glass vessels. He showed that such a liquid as ether could be converted wholly into vapour, notwithstanding the existence of an enormous pressure, in a volume less than twice the volume of the liquid from which it was produced. He also observed that there was a definite temperature, independent of the actual amount of ether present, above which the liquid meniscus could not be observed, an indication that ether cannot exist as liquid above a certain temperature. Similar results were obtained with a number of other liquids, but their significance was not generally recognised at the time. Faraday, however, realised that the reason why he was unable to liquefy certain gases was that they were probably in the same condition as the ether vapour in Cagniard de la Tour's experiments when heated above the temperature at which the liquid meniscus disappeared, in which case he added that 'no compression, without the conjoint application of a degree of cold below that we have as yet obtained, can be expected to take from them their gaseous state.' It is curious, therefore, that Faraday made no attempt to realise the Cagniard de la Tour's state with any of the gases he had succeeded in liquefying.

Andrews found that on compressing carbon dioxide in a glass capillary tube at temperatures below 30·9°C., the volume diminished more rapidly than would be indicated by Boyle's Law, until at a certain pressure, depending on the temperature, liquefaction commenced. The pressure then remained constant while the volume was being diminished, until liquefaction was complete. After this, a large increase in pressure again became necessary in order to diminish the volume further. At temperatures above 30·9°C., however, he could obtain no indications of liquefaction at all, whatever pressure was applied. On partially liquefying carbon dioxide, and slowly raising the temperature, the surface of demarcation between the liquid and gas became fainter, lost its curvature, and finally disappeared at 30·9°C. The space was then occupied by a homogeneous fluid which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass.

From these results on carbon dioxide and from analogous results for nitrous oxide, Andrews concluded that there is a perfect continuity between the gaseous and liquid states, and that for each gas there is a definite temperature above which it cannot be condensed to the liquid state. This temperature he called its *critical temperature*. The 'Cagniard de la Tour point,' to which Faraday frequently referred, and the 'absolute boiling-point' of Mendeléeff, correspond to the same temperature. The pressure required to effect liquefaction at the critical temperature is called its *critical pressure*.

Andrews was able from his results to draw a rational distinction between a 'vapour' and a 'gas' by defining them as gaseous substances respectively below and above their critical temperatures.

As a result of the work of Andrews it is clear that the general nature of the isothermals



DIREOTOR OF IN
Bengal

FIG. 1.

for a gas over a range of temperature, including the critical point, is similar to that shown in Fig. 1. Each isothermal below the critical point consists of three distinct parts, the middle portion being horizontal. The abscissæ of its extremities, *e.g.* v_v and v_l on the T_0 isothermal, represent the specific volumes of the substance, if the diagram refers to unit mass, as saturated vapour and as liquid under its own vapour pressure at T_0 respectively; intermediate volumes correspond to mixtures of liquid and vapour.

The theory of Andrews, that the change from gas to liquid is continuous, and that there is no essential difference between the two states, was adopted by Van der Waals, who, in 1879, put forward an equation to represent the behaviour of any fluid that does not change its molecular complexity on passing from the gaseous to the liquid state (Van der Waals, Die Continuitat des gasformigen und flussigen Zustandes).

The characteristic equation for a perfect gas

$$pv = RT$$

(where p, v, and T denote pressure, volume, and absolute temperature respectively, and R is a constant) represents the behaviour of ordinary gases accurately only over a small range of pressure, and at temperatures sufficiently removed from the critical point. As p increases, at constant temperature, from atmospheric pressure to one or two hundred atmospheres, the compressibility is initially greater than Boyle's Law indicates, the product pv diminishing as p increases (Regnault, Mém. de l'Acad. 21, 329; Amagat, Ann. Chim. Phys. 1880, [v.] 19, 345; 1881, [v.] 22, 353; 1883, [v.] 28, 456, 464; 1893, [vi.] 29, 68). The value of pv reaches a minimum, and afterwards increases with increase of pressure, so that at extremely high pressures all gases are much less compressible than is expressed by Boyle's Law (Natterer, *l.c.*; Amagat, *l.c.*). The initial diminution in the value of pv for a gas becomes less marked with rise of temperature, and at a sufficiently high temperature it is not observed. In the cases of hydrogen, helium and neon, this temperature, although considerably above the critical point, is much below the ordinary temperature, and the values of pv for these gases at this temperature steadily increase with rise of pressure from atmospheric pressure upwards (Regnault, Amagat, *l.c.*; Wroblewski, Monatsh. 1888, 9, 1067; Witkowski, Bull. Acad. Sci. Cracow, 1905, 6, 305; Kamerlingh Onnes and Braak, Comm. Phys. Lab. Leyden, 1907, No. 97; Burt, Trans. Faraday Soc. 1910, 6, 19).

These results can be represented fairly accurately by the equation of Van der Waals,

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

the magnitudes of the (small) constants a and b (which may be deduced from the experimental values for p, v, and T) depending respectively upon the extent to which the molecules of the gas attract one another and upon their actual volume. This equation, besides representing the behaviour of compressed gases fairly accurately, also gives some account of the relationship between the liquid and gaseous states.

The equation represents the isothermals of a gas over a range of temperature including the critical point as being of the form shown in Fig. 1, with this difference, that those isothermals below the critical isothermal have the horizontal portions replaced by wavy curves, as indicated in the diagram by BCDEF on the isothermal for T_0°. The passage from vapour to liquid is thus represented as a continuous process. The portions BC and EF of the curve correspond with the conditions of superheated liquid and supersaturated vapour respectively, but the portion CDE of the curve, where p and v increase or decrease together, cannot be experimentally realised. At the critical point the specific volumes of vapour and liquid are identical, and the wavy portion of the curve therefore vanishes. Therefore the tangent at the critical point is horizontal, *i.e.* $dp/dv=0$. Since, moreover, the curvature of the critical isothermal changes sign at the critical temperature, $d^2p/dv^2=0$. These two relations give

$$2av_k^{-3}=RT_k(v_k-b)^{-2} \text{ and } 3av_k^{-4}=RT_k(v_k-b)^{-3}$$

the suffixes denoting critical values; whence

$$v_k=3b \text{ and } T_k=8a/27bR$$

Substituting in the original equation, $p_k=a/27b^2$. The critical constants for carbon dioxide, calculated by Van der Waals from these formulæ, were $T_k=32{\cdot}5$C., $v_k=0{\cdot}0069$, $p_k=61$ atmos., in fair agreement with the experimental values 30·9°C., 0·0066 and 70 atmos. respectively. The critical constants for hydrogen were determined by Wroblewski (Monatsh. 1888, 9, 1067) in a similar manner from his observations on the compressibility of the gas at low temperatures; his results agree remarkably well with the experimental values (Dewar, Chem. News. 1900, 81, 136) and afford a good instance of the utility of Van der Waals' theory. For further information concerning Van der Waals' equation, see Nernst's Theoretical Chemistry.

Liquefaction of the so-called 'permanent gases.'—The liquefaction of the five or six gases which Faraday and others had been unable to liquefy, and which had been called the 'permanent gases,' was, in the light of Andrews' researches, seen to depend upon the production of extremely low temperatures, since the lowest temperatures previously obtained had been above their critical points.

The first successful attempts to effect their liquefaction were made in 1877. On December 24th of that year, at the meeting of the French Academy, it was announced that Louis Cailletet of Chatillon-sur-Seine had liquefied both oxygen and carbon monoxide, whilst Raoul Pictet of Geneva had succeeded in liquefying oxygen (Compt. rend. 1877, 85, 1214, 1217, 1220).

The method used by Pictet (Compt. rend. 1877, 85, 1214; Ann. Chim. Phys. 1878, [v.] 13, 145; Arch. des Sci. Phys. et Nat. 1878) is essentially that devised by Faraday. Oxygen was generated by heating potassium chlorate in a wrought-iron flask. A long steel tube, provided at one end with a stop-cock, was attached to the flask. The accumulation of oxygen in the retort and tube created a pressure of 500 atmospheres. The tube was cooled to −120° to −140°, which is below the critical temperature of oxygen, by surrounding it with a copper cylinder through which liquid carbon dioxide, boiling under reduced pressure, was circulated. The liquid carbon dioxide was obtained by compressing the gas to 4-6 atmospheres, and cooling it externally by means of liquid sulphur dioxide, boiling under diminished pressure at −65°C. The elaborate apparatus employed was so designed that both sulphur dioxide and carbon dioxide could be liquefied, evaporated and re-liquefied repeatedly, so as to produce *continuous cooling*. The oxygen liquefied in the cooled tube, and when the stop-cock was opened, issued as a liquid jet with great violence, since the pressure employed was far in excess of that actually necessary for liquefaction.

The simple apparatus employed by Cailletet (Ann. Chim. Phys 1878, [v.] 15, 132) is shown in Fig. 2. The gas is introduced into a glass tube, TP, the narrow end of which consists of a stout capillary tube By means of a metal collar, A, and the nut E′, the tube is screwed into a strong steel cylinder, B, partially filled with mercury. To compress the gas, water is forced into the steel cylinder by a hydraulic pump, through the copper tube U, which is fastened by the screws R and F into the apparatus; a pressure of several hundred atmospheres can thus be applied A glass jacket M, and a bell-jar C, supported on the plate S, surround the capillary tube. The tap *r* serves to run off any liquid refrigerant in the jacket M.

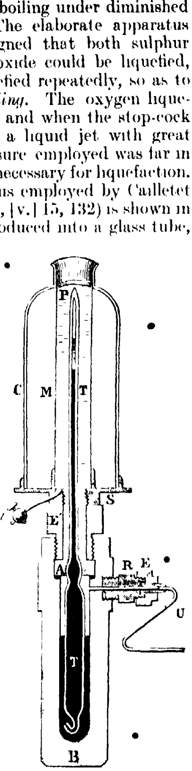


FIG 2.

With this apparatus Cailletet liquefied acetylene (Compt. rend. 1877, 85, 851) and nitric oxide (*ibid.* 85, 1016), the latter condensing at −11° under a pressure of 104 atmospheres. Methane was not liquefied at 7° under a pressure of 180 atmospheres; but by suddenly releasing the pressure, the temperature of the gas was reduced sufficiently for liquefaction to occur, and a fine mist of liquid methane was formed in the tube. This method was successfully applied to oxygen and carbon monoxide (*ibid.* 85, 1213). The gases were compressed to 300 atmospheres, and cooled to −29°. The pressure was then suddenly released, when the resultant cooling effect was sufficient in both cases to produce partial liquefaction, a mist being formed of minute liquid droplets.

The theory of the process is simple. When a gas expands against external pressure, it performs work. This work is accomplished at the expense of the internal energy of the gas, and a diminution in the internal energy means a fall in temperature. To obtain the greatest fall in temperature possible, it is essential to perform the expansion with great rapidity in order that there may be no appreciable time for the gas to acquire heat from its surroundings. The fall in temperature experienced by a perfect gas when it expands adiabatically from an initial pressure p_1, at absolute temperature T_1, to a final pressure p_2, is given by $T_1 - T_2$, where

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}}$$

(k denoting the ratio of the specific heats of the gas). In the case of air, where $k = 1{\cdot}41$, if p_1, p_2, and T_1 were 100 atmospheres, 1 atmosphere, and 273° abs. respectively, the final temperature T_2 should be 71·5° abs., or −201·5°C. Although this numerical result is necessarily somewhat inaccurate, owing to the fact that air under the above conditions deviates considerably from the laws of a perfect gas, it is sufficient to indicate that the adiabatic expansion of a gas is capable of producing extremely low temperatures. In Cailletet's experiments, expansion occurred practically under adiabatic conditions.

By this method Cailletet also succeeded in liquefying air and nitrogen, and obtained indications of the liquefaction of hydrogen (Compt. rend. 1877, 85, 1270). He also prepared liquid ethylene, first obtained by Faraday, in large quantities, and recommended its use as a refrigerant (Compt. rend. 1882, 94, 1224; 1883, 97, 1115; Ann. Chim. Phys. 1883, [v.] 29, 153). By cooling compressed methane and oxygen with this reagent boiling under diminished pressure, Cailletet obtained liquid methane and oxygen in the static form (Compt. rend. 1884, 98, 1565; 1885, 100, 1033).

A period of great activity in connection with the liquefaction of gases followed the publication of the successful pioneering experiments of Pictet and Cailletet, the subject being taken up by Wroblewski and Olszewski in Cracow, by Dewar at the Royal Institution in London, and by Kamerlingh Onnes at Leyden. The Polish physicists occupied themselves mainly in determining the physical constants of liquefied gases. To obtain low temperatures, they acted upon Cailletet's suggestion, and employed liquid ethylene, which boils at −102°C., as a refrigerant. They compressed oxygen, nitrogen, and carbon monoxide in a stout glass tube by means of a modified Cailletet pump and cooled the gases to −136° by the rapid evaporation under diminished pressure of liquid ethylene, previously cooled with Thilorier's mixture. Under a pressure of 22·5 atmospheres, oxygen readily liquefied. The liquefaction of the other two gases was only effected by compressing them to 150 atmospheres at −136°, and then slowly reducing the pressure, when a further cooling effect was obtained. In each case a transparent liquid, with a well-defined meniscus, was obtained (Wied. Ann. 1883, 20, 243; Compt. rend. 1883, 96, 1140, 1225; Monatsh. 1883, 4, 415). The later work of these investigators was published separately. Wroblewski, who reached the temperature of −152°C. by rapidly evaporating liquid ethylene, obtained considerable quantities of liquid oxygen; he solidified nitrogen and carbon monoxide, and obtained temperatures below −200° by the rapid evaporation of the corresponding liquids; studied the utility of liquid methane as a refrigerant; obtained indications of the liquefaction of hydrogen; and at the time of his death was engaged in a

study of the compressibility of hydrogen over a wide range of pressure and at very low temperatures (Wroblewski, Compt. rend, 1883, 97, 166, 309, 1553; 1884, 98, 149, 304, 982; 99, 136; 1885, 100, 979; 1886, 102, 1010; Wied. Ann. 1883, 20, 860; 1885, 25, 371; 1885, 26, 134; 1886, 29, 428; Monatsh. 1885, 6, 304).

The independent investigations of Olszewski, in which he solidified ethylene, carbon monoxide, nitrogen, and methane; liquefied oxygen in quantity and used the liquid as a refrigerant; obtained indications of the liquefaction of hydrogen and determined the physical constants of these and other gases, were summarised by himself in 1895 (Phil. Mag. 1895, [v.] 9, 188; 40, 202; *cf.* Compt. rend. 1884, 98, 365, 913; 1884, 99, 133, 184, 706; 1885, 100, 350, 940; 1885, 101, 238; Monatsh. 1884, 5, 124, 127, 1886, 7, 371; 1887, 8, 69; Ann. Phys. Chim. 1889, [ii.] 37, 327; 1895, [ii.] 56, 133).

The work of Dewar at the Royal Institution, from 1880 to 1895, led to the production of liquid air, oxygen, &c., in large quantities by using a liquefying plant constructed of metal and utilising liquid ethylene as refrigerant (Proc. Roy. Inst. 1886, 550; *cf. ibid.* 1884, 148; Phil. Mag. 1884, [v.] 18, 210). Dewar commenced a study of the properties of matter in general at low temperatures, and in this connection he made a most valuable contribution towards the manipulation of liquefied gases by introducing a vessel in which they could be kept with the minimum of loss by evaporation. The *Dewar flask* (Fig. 3) is simply a double-walled flask of convenient shape, from the space between the walls of which the air has been exhausted. The contained liquid is thereby separated from the atmosphere by a vacuum-jacket except at the mouth of the flask. Evaporation of liquid air and similar liquids in these flasks takes place only very slowly, since the heat radiated across the vacuous space is only one-seventh of the total heat which would reach the inner vessel were the jacket to contain air. If desired, the flasks may be silvered on the inside, thus increasing their efficiency (*cf.* Briggs, Proc. Roy. Soc. Edinburgh, 1922, 41, 97).

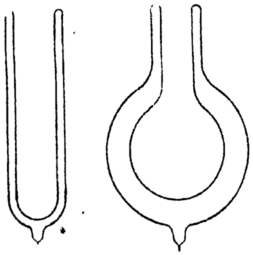


FIG. 3.

The method of self-intensive refrigeration (so-called regenerative process).—The experiments of Wroblewski, Olszewski, and Dewar on the production of low temperatures, previously described, involved no new principle; the 'cascade' method of lowering the temperature by stages, originated by Pictet, had been employed, and at times combined with Cailletet's expansion method. In 1895 a new principle, that of producing cold by self-intensive refrigeration, was introduced almost simultaneously by Hampson and Linde. Briefly, it consists in continuously supplying the gas to be liquefied to an apparatus in which it may be cooled by expansion, and utilising each portion of gas, after it has been expanded and cooled, in lowering the initial temperature of the gas about to be expanded, until the cumulative effect of the cooling process is sufficient to produce liquefaction. For this purpose, the highly compressed gas at the ordinary temperature is passed downwards through a long copper spiral tube, expanded through a throttle valve, and the issuing gas passed upwards over the exterior of the copper tube.

For a description of Linde's liquefying plant *v.* the Engineer, October 4, 1895; J. Soc. of Arts, 1897, 1091; *cf.* also Eng. Pat. 12528, 1895; Ann. Phys. Chem. 1895, [ii.] 57, 328; Ber. 1899, 32, 925).

The general arrangement of Hampson's air-liquefying plant is indicated in Fig. 4. Air is

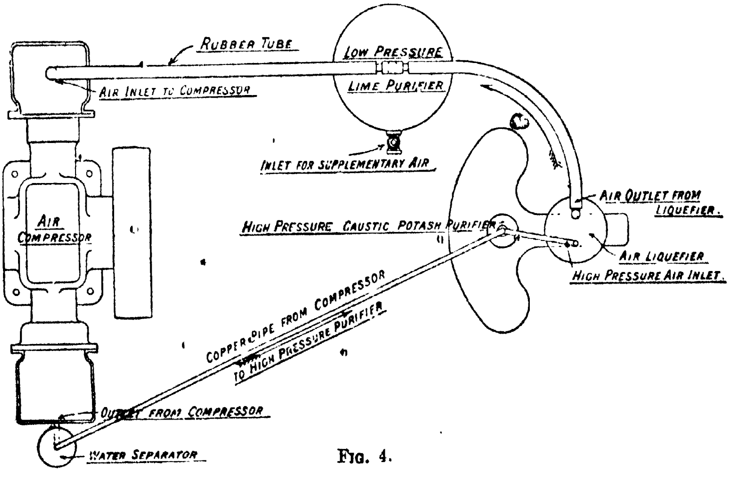


FIG. 4.

drawn into the compressor through the large purifier, containing slaked lime to absorb carbon dioxide, and compressed in two stages to 150–200 atmospheres. The compressor is water-cooled to remove the heat generated by compressing the air. The air is then forced through a separating vessel, in which most of the water used as lubricant separates out, and afterwards through the high-pressure purifier containing potassium hydroxide, in which the remaining water and carbon dioxide are completely absorbed. The purified air then enters the liquefier; that which passes out is usually returned through the low-pressure purifier to the compressor, and used again. The purifiers do not then have to be very often refilled.

The Hampson liquefier, manufactured by the British Oxygen Co. (Eng. Pat. 10165, 1895; 7773, 1898; J. Soc. Chem. Ind. 1898, 17, 411), is shown in section in Fig. 5. In designing it, the following points were kept in view: the necessity for having a large, exposed surface of material of high thermal conductivity between the compressed and expanded air, the thickness of the material being diminished as far as possible; the desirability of having both compressed and expanded air in small masses in close contact with the conducting material, and of reducing the total mass and volume of this heat interchanger to the smallest possible amount, in order to minimise the mass of metal to be cooled down with the gas, and prevent, as far as possible, any access of heat from the surroundings. The liquefier consists of four copper coils, B, wound co-axially about a spindle, D, and joined at their lower ends to a valve, C, which may be opened or closed by turning the hand wheel E attached to the top of the spindle. A metal chamber, G, soldered directly to the casing of the coils, serves to collect the liquid air. The whole is enclosed in a metal chamber and the space between this jacket and the casing of the coils is filled with non-conducting material.

The purified air, the pressure of which is indicated by the gauge O, enters the liquefier through A, travels down the coils and is allowed to escape through the valve C. The released air immediately expands down to approximately atmospheric pressure, and travels back over the exterior of the coils B, finally passing back into the compressor or directly into the atmosphere. The expanded air acts with a self-intensifying cooling effect on the compressed air which is passing down through the coils, and in from 6 to 10 minutes part of the air begins to liquefy and collect in G. This receiver is emptied by turning the wheel T, which opens the valve P, when the liquid flows down the hollow spindle R into a vacuum receiver. A gauge H, connected by the tube J with the receiver G, indicates the amount of liquid in G. About 1½ litres of liquid air per hour can be obtained with an ordinary Hampson apparatus, and no auxiliary refrigerant is required. The interchanger acts so perfectly that the air which leaves the apparatus is only about 1° colder than that which enters it. About 5 p.c. of the air passing through the apparatus is liquefied.

In the liquefying machines of Hampson and Linde, the work done against atmospheric pressure as the gas flows along after expansion is not performed by the gas at the expense of its internal energy; the necessary energy is continuously supplied by the compression pump. A steady stream of gas at high pressure is pumped continuously into the coils of the liquefier, and after passing through the valve, is converted into a steady stream of gas at low pressure. There is a slight thermal effect due to the performance of external work, but its magnitude only depends upon the extent to which Boyle's Law is in error in representing the compressibility of the gas. It may be calculated from a knowledge of the specific heat of the gas and its compressibility, and at ordinary temperatures amounts to a slight cooling effect with all gases except hydrogen, helium, and neon. The main thermal change, however, is due to free expansion of the gas, and work is done in increasing the mean distance between the molecules of the gas in opposition to the forces of molecular attraction. This is performed

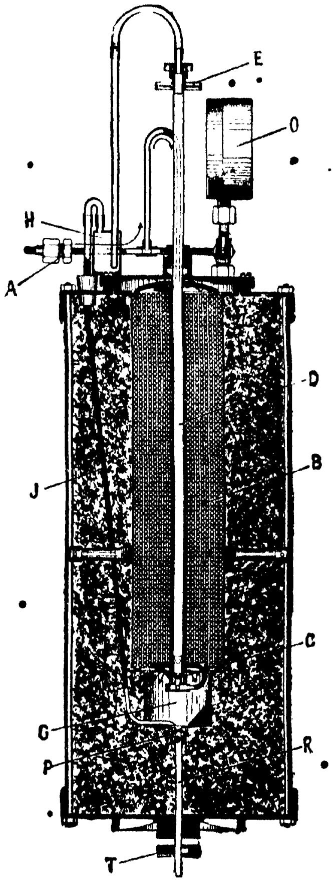


Fig. 5.

at the expense of the internal energy of the gas. The subject was studied experimentally by Joule and Thomson (Phil. Trans. 1853, 143, 357; 1854, 144, 321; 1862, 152, 579) for a number of gases, and a slight cooling effect was found to be the net result in each case at ordinary temperatures except for hydrogen. The fall in temperature was proportional to the fall in pressure (up to 6 atmospheres), and varied approximately as the inverse square of the absolute temperature. At 17·1°C. the fall in temperature for air is 0·255°C. per atmosphere.

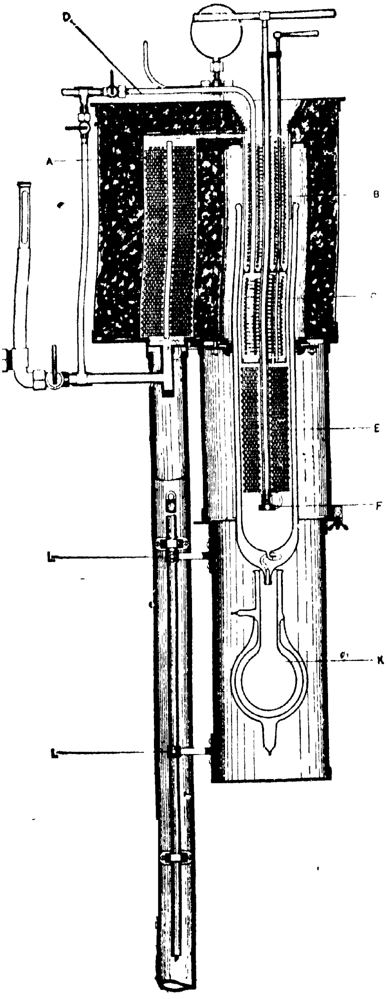


FIG. 6.

There is a temperature at which the thermal effect produced by free expansion (the Joule-Thomson effect) is zero. According to Olszewski (Phil. Mag. 1902, [vi.] 3, 535) this is −80·5°C. for hydrogen, and below this temperature hydrogen is also cooled by free expansion. The 'inversion temperatures' in the case of air and nitrogen are considerably higher than ordinary temperatures, and appear to vary with the initial pressure of the gas (Olszewski, Bull. Acad. Sci. Cracow, 1906, 792).

To liquefy hydrogen (and helium) it is therefore necessary to cool the gas strongly before applying the self-intensive cooling process. It was by this means that Dewar (Chem. News, 1900, 81, 136) first succeeded in collecting liquid hydrogen. Travers (Phil. Mag. 1901, [vi.] 1, 411) and Olszewski (Bull. Acad. Sci. Cracow, 1902, 619; 1903, 241) have since described modified Hampson liquefiers for preparing liquid hydrogen, in which the hydrogen is cooled by liquid air and then allowed to expand through a specially constructed valve. By cooling helium to the temperature of liquid hydrogen and then applying the self-intensifying process, Kamerlingh Onnes (Compt. rend. 1908, 147, 421; Proc. K. Acad. Wetensch. Amsterdam, 1908, 11, 168) succeeded in obtaining helium in the liquid state.

The hydrogen liquefier designed by Travers and manufactured by the British Oxygen Company, is shown in Fig. 6. Pure dry hydrogen at 150–200 atmospheres pressure, enters the lower end of the coils A and is cooled by the cold hydrogen returning to the gas-holder. It then passes into the top of the coils in the chamber B, which is filled with liquid air, and by the time it has reached the bottom of the coils it is cooled to −190°C. The cold gas has its temperature lowered to below −200°C. as it passes through the coils in chamber C, which is connected by the pipe D to a vacuum pump, and in which liquid air is boiled under diminished pressure. The hydrogen then expands through the valve F at the end of the regenerator-coil E. The cooling-effect is self-intensified in the usual way, the cooled gas passing upwards over the coils E, and the outsides of the chambers B and C, finally cooling the coil A as it passes out of the apparatus. The coils B, C, and E are enclosed in a large, silvered vacuum-jacket. Liquid hydrogen collects in the vacuum vessel K, which is enclosed in a special box, hinged at LL to the supporting column and provided with glass windows.

Claude's process for liquefying gases.—The cooling effect produced when a gas expands with the performance of external work is much greater than that which is produced by the free expansion of the compressed gas. Mechanical difficulties for many years prevented this cooling effect from being intensified by rendering the process continuous, but it has now been effected by Claude. The process, as worked by Claude for the liquefaction of air, consists in compressing the air to 40 or 50 atmospheres and dividing it into two portions. One of these is expanded in a cylinder to 4 or 5 atmospheres, performing external work and thereby becoming cooled, and this cold air is then used to cool the other part, which can be thereby liquefied. This method, when applied on a large scale, needs less power than the Linde process; moreover, it may be used as a means of producing a low temperature preparatory to applying the ordinary self-intensive refrigeration method

(Claude, Compt. rend. 1900, 131, 500; 1902, 134, 1568; 1905, 141, 762, 823; Eng. Pat. 27658, 1902; Fr. Pat. 322107, 1902; Linde, J. Soc. Chem. Ind. 1911, 30, 744). For further information concerning Linde and Claude's processes, *v.* OXYGEN.

Literature.—Hardin's Rise and Development of the Liquefaction of Gases; Sloane's Liquid Air and the Liquefaction of Gases; Ewing's Mechanical Production of Cold; Travers' Study of Gases; Preston's Theory of Heat; &c.

LIQUEURS and **CORDIALS.** The general characters of these beverages have already been described under the heading CORDIALS AND LIQUEURS (vol. II.), the former term being usually applied to British preparations and to such as have only one characteristic flavouring ingredient, and the latter to the foreign varieties which are usually of a more complex character. The term *liqueur* is also applied to certain wines and spirits remarkable for their bouquet as 'Tokay,' 'Liqueur brandy,' &c. *Bitters* are generally classed commercially with liqueurs and cordials, and contain one or more ingredients supposed to possess tonic and medicinal properties.

In ancient times, liqueurs consisted merely of wine flavoured with spices (as cinnamon) and sweetened with honey, and in the Middle Ages various aromatic herbs (as absinth, hyssop, &c.) were employed in a similar manner, the product being known as 'wine of herbs.' The 'liquori' of Italy were, however, the true prototypes of the modern liqueur, as the Italians were the first to extract the aromatic principles of the roots, leaves, flowers, fruit, and seeds of plants by means of spirit. Sometimes gold or silver leaf in a finely divided state was added to the liqueur, not only to give lustre, but also because of certain medicinal virtues these metals were supposed to possess.

At the present time, France is *par excellence* the home of the liqueur, and some of the most celebrated varieties have originated at certain monasteries which formerly derived considerable revenues from their manufacture and sale, *e.g.* *Bénédictine*, *Chartreuse*, *Trappistine*, &c. Other countries have their special preparations as *Anisette d'Hollande* and *Crême de Genièvre* (Holland), *Allasch* and *Kummel* (Russia), *Alkermès* (Italy), *Maraschino* (Dalmatia), and the various *Cocktails* of the United States of America.

The number and variety of liqueurs and cordials is very great but the best known are comprised in the following list:—

Absinth
Advocaat
Alkermes
Allasch
Angostura (bitters)
Anisette
Bénédictine
Brandy (cherry, &c.)
Chartreuse
Clove cordial
Cocktails (American)
Crême de Menthe
Curaçoa
Gin (sloe, &c.)
Kirsch
Kümmel
Maraschino
Noyau
Parfait Amour
Peppermint cordial
Ratafias
Trappistine
Vermouth
Whiskey (cherry, &c.)

In the manufacture of liqueurs, the purity and good quality of all the ingredients used is a matter of the first importance. The spirits should be highly rectified spirits of wine as free as possible from fusel oil and free acid; the sugar of the finest white crystals or sugar-candy made into a clear syrup with distilled or pure soft water; glycerol (when employed) should be highly refined and colourless; and all the flavouring ingredients (*e.g.* flowers, fruits, rinds, roots, seeds, &c.) should be sound and well-dried.

The simplest method of manufacture, adopted for the commoner kinds of liqueurs, is that of merely adding essential oils to the spirit, and then the necessary amount of sugar syrup or glycerol.

The essential oils should be recently distilled and dissolved in from 5 to 10 times their weight of alcohol before being added. The particular flavour required can thus be better attained and cloudiness or milkiness of the finished liqueur avoided.

The finer qualities, however, are made by macerating the flavouring ingredients in spirit of about 85° to 90° alcohol by volume and distilling the infusion. The distillation was formerly conducted in copper stills heated by direct fire, then double-bottomed coppers were employed, and subsequently a water-bath added, but now steam-jacketed stills only are used in the largest liqueur factories. The middle portion of the distillate is used for the finest liqueurs, the first fractions being rough and the last inferior in character. Syrup is added and sometimes glucose or glycerol to give density and impart a 'velvety' character to the liqueur, and the whole is heated, well mixed and diluted with water, after which filtration and 'fining' may be found necessary.

Liqueurs are often classified in France according to the proportions of spirit and sugar used, *e.g.* 'crêmes,' 'huiles,' or 'baumes,' which are heavily sweetened to a thick oily consistency, and 'eaux,' 'elixirs,' and 'extraits,' which are perfectly limpid and less highly sweetened. As a rule, the same proportions are employed for the same quality of liqueur. The following grades may be taken as typical:—

	Ordinaire	Demifine	Fine	Surfine
Alcohol at 85°	25 litres	28	32	36
Sugar	12½ kilos	25	37½	50
Water	67 litres	57	46	34

It will be observed that in the superior grades the proportions of alcohol and sugar are increased with a corresponding diminution in the proportion of water.

The flavouring ingredients are extremely numerous and varied in character, and their nature and proportions used are jealously guarded by the manufacturers as trade secrets.

The essential principles are extracted by *infusion* with hot spirit (if the aromatic principle is not too volatile), the ingredients being first moistened with boiling water; or by *maceration* with cold spirit which may require hours, days, or even many months, according to the solubility of the essential principles; by *digestion* or prolonged infusion or maceration in hermetically closed vessels when the aromatic principles are extracted only with difficulty by cold alcohol; or by *distillation* when only the natural essential oils or other volatile flavouring constituents are required. The following plants should always be distilled by steam: *absinth*, *anise*, *balms*, *caraway*, *citronella*, *fennel*, *juniper*, *hyssop*, *lavender*, *melilot*, *mint*, *orange*, *rose*, *sage*, and *thyme*.

Aromatic tinctures for use in flavouring liqueurs are sometimes prepared by a kind of fractional filtration. The ingredients in a finely divided state are made into a paste with spirit and placed in a large funnel plugged with cotton-wool. Alcohol is poured in and the extract allowed to filter through drop by drop. The first portions are the purest and strongest, those following decreasing in flavour until the latter becomes too weak or even foreign in character.

Careful *mixing* is essential to the successful manufacture of liqueurs. Two separate vessels should be employed, the one for the essences or flavouring ingredients dissolved in about three-quarters of the total amount of alcohol required by the formula, and the other containing the syrup together with the rest of the alcohol. In this way the danger of the aromatic principles being thrown out of solution on the addition of the syrup is obviated, and the process of clarification expedited. The admixture should always be made in the cold to avoid loss of the flavouring principles, and the vessels may be hermetically sealed and provided with a scale or gauge rod to indicate the quantity of the ingredients admixed. The liqueur should rest for some days after mixing, and any defects, detected by taste, remedied before colouring, clarifying, or filtering.

Filtration, when necessary, should be conducted as quickly as possible. The older methods with cotton, paper, or wool in copper or tin filters are slow and result in loss of spirit and flavour. A better method is to use paper-pulp brought to the consistency of thick soup with some of the liqueur to be cleared. This is added to the bulk of the liqueur and the whole passed through a hair sieve. Natural clearing is best if time permits.

Clarification or '*collage*' with 'fining' materials is best avoided if possible, but is often necessary. The principal materials and the proportions used are as follows: *albumen*, white of egg (one egg for every 10 litres); *gelatin* (30 grams per 100 litres); *isinglass* (10 grams per 100 litres); *milk* (1 litre boiled in 100 litres, with 15 grams of alum). Animal or vegetable carbon, alum, nitre, and various 'filtering powders,' as 'Poudre Lebeuf,' are also employed. For coloured liqueurs, which are apt to suffer by this treatment, filtration is preferable to 'collage.'

Liqueurs containing various flavouring ingredients improve by keeping, as time is required for the intimate blending of the various substances in solution. The effect of this 'maturing' is artificially brought about in ordinary liqueurs and those intended for immediate use by a process known as *tranchage*, which consists either in heating in a water-bath to about boiling-point, or by successive coolings with ice. The object is to suppress the penetrating flavour of the new spirit and to give a smooth uniform character to the product so that none of the different flavouring ingredients can be individually recognised. Tranchage should be carried out *before* the coloration, clarification, or filtration of the liqueur.

The place of *storage* of liqueurs should be kept at a uniform temperature of 15° to 20° and the liqueurs protected from strong light or direct sunshine, as this affects the colour, frequently causing it to change or to be precipitated.

Bitters are considered to be tonic and stomachic and to improve the appetite when taken in moderation. They are prepared by maceration without distillation. The substances most commonly used are cascarilla, gentian, orange peel, quassia and wormwood. The best known preparations are *Angostura*, *Khoosh*, *orange*, and *peach bitters*. A fundamental principle in most bitters is gentian. A bitter made according to the following formula, which represents the proportions necessary to make 20 gallons, may be taken as typical: 6 lbs. gentian; 5 lbs. cinnamon; 5 lbs. caraway seeds; 1 lb. juniper berries; ½ lb. cloves. Macerate in spirit of about 90° (or 60 p.c.) for 10 or 12 days; strain, filter, add a syrup consisting of 10 lbs. of sugar to 13 gallons of water, and colour with cochineal.

English bitters may be made by digesting 5 ounces of the outer rind of dried orange peel, 6 ounces of cinchona bark, 6 ounces of gentian, 8 ounces of *Carduus benedictus*, 8 ounces of centaury, 8 ounces of wormwood, and 4 ounces of orris root, with 12 gallons of spirit about proof strength, filtering and sweetening with 12 lbs. of sugar

In the following brief description of the best known liqueurs and cordials, the formulæ given are not intended, in the case of proprietary articles, as *Angostura*, *Chartreuse*, &c., to represent the exact composition or mode of preparation of the liqueurs originally known under these names, and the manufacture of which is carefully preserved as trade secrets, but only to serve as a guide to the preparation of a more or less successful imitation or substitute in each instance.

Absinth (*v.* article ABSINTH in vol. 1.).

Angostura. A well-known 'bitters' originally made by the Capuchin Friars' Mission on the river Caroni in South America, and called after the ancient name of a city in Venezuela, now Bolivar.

As originally made the essential bitter principle was extracted from the bark of a plant belonging to the order *Rutacea*, genus *Galipea*, which has valuable febrifuge properties. The following formula is taken from the Scientific American Cyclopædia, 1903: 4 oz. gentian root; 10 oz. each of calisaya bark, Canada snake root, Virginia snake root, liquorice root, yellow bark, allspice, dandelion root, and Angostura bark; 6 oz. cardamon seeds; 4 oz. each of Tolu balsam, galanga, and Turkey rhubarb; 1 lb. each of orange peel and alkanet root; 1½ oz. each of caraway seed and cinnamon; ½ oz. cloves; 2 oz. each of catechu, coriander seed, nutmegs, and wormwood; 1 oz. mace; 1¼ lb. red sanders wood and 8 oz. turmeric. The ingredients are pounded and macerated for 15 days in 50 gallons of proof spirit, 30 lbs. of honey added, and filtered. This formula does not purport to represent the composition of 'Angostura Bitters' as made to-day, which is the registered title of a proprietary article, the ingredients in which have not been made known.

Advocaat, a spirit made in Holland from spirit and yolk of eggs and sweetened with sugar. The average strength is about proof.

Alkermes, a liqueur originally made at Florence and highly esteemed in the South of Europe. The original formula for the Alkermes de S. M. Novella is as follows: Bay leaves and mace, 1 lb each; nutmegs and cinnamon, 2 oz. each; cloves, 1 oz. all bruised; cognac brandy, 3½ gallons; macerate for 3 weeks with frequent agitation. Distil over 3 gallons; add 18 lbs. of clarified spirit of kermes and 1 pint of orange flower water, mix well and bottle.

Allasch, a superior kind of kummel (*q.v.*) flavoured with caraway seeds, bitter almonds, angelica root, anise, iris root, and orange peel. It is usually supersaturated with sugar which crystallises out in the finished liqueur. Strength about 25 u.p. or 43 p c. alcohol by volume.

Anisette. The principal varieties, differing somewhat in the flavourings used, are *Anisette d'Amsterdam* and *Anisette de Bordeaux*. This liqueur may be made as follows: 4 oz. aniseed; 1 oz. each of coriander and sweet fennel seeds bruised; ½ gallon of rectified spirits and 3 quarts of water. Macerate 5 or 6 days, distil over 7 pints and sweeten with 2½ lbs. of pure sugar. The alcoholic strength of anisette is usually about 52 p.c. of proof spirit or approximately 30 p c. of absolute alcohol by volume.

Bénédictine, so called from a monastery of this order in the north of France where the liqueur was first made. It is now produced on a large scale by a company at Fécamp, at a uniform strength of 75 p.c. proof spirit or 43 p.c. of alcohol.

This liqueur may be prepared by the following formula: cloves, 2 grams; nutmegs, 2 grams; cinnamon, 3 grams; balm, peppermint, freshly gathered angelica and genepi of the Alps, each 25 grams; calamus, 15 grams; cardamoms (small), 50 grams; arnica flowers, 8 grams. The materials are crushed and macerated for 2 days in 4 litres of alcohol at 85°; 3 litres of water added and the whole distilled, taking over 4 litres. A cold syrup made with 4 kilos. of sugar and 2 litres of water is added, the mixture brought up to 10 litres with water, coloured, and filtered

Brandy (apricot, cherry, ginger, lemon, orange, peach, raspberry, &c.) by macerating the fresh fruits often for prolonged periods or mixing the juice with brandy, and sweetening with sugar syrup. Frequently essential oils are used, as ginger-brandy oil, essence of lemon, &c., and plain spirit instead of grape brandy. *Gin* and *whiskey* are similarly used for the preparation of fruit liqueurs, as sloe gin, cherry whiskey, &c., and, as in the case of brandy liqueurs, plain rectified spirit is commonly employed instead of gin or whiskey.

Chartreuse (*see* vol. I.).

Cocktail, a compounded drink much used in America. The spirit basis is brandy, gin, whiskey, or other spirits, and the different varieties, depending upon the kind of flavouring used, are very numerous and sold under fanciful names. A bottle of brandy cocktail may be made as follows: one-half brandy; one quarter water; and a wineglassful each of bitters, curaçoa, and gum syrup. Whiskey and gin cocktails may be made by the same recipe, substituting these spirits for brandy. The strength is usually from 50 to 75 p.c. of proof spirit.

Clove cordial may be prepared by the following formula: Bruised cloves, 1 oz. or essential oil, 1 dram to every 4 gallons of proof spirit. If distilled, this should be done over a quick fire. The necessary deep colouring is sometimes obtained by means of poppy flowers or cochineal, but more commonly with brandy colouring or red sanders wood. The cordial is improved by the addition of 1 dram of bruised pimento or 5 drops of the oil for every ounce of cloves. It is sweetened with about 3 lbs. of sugar to the gallon.

Crême de Menthe is one of the most popular liqueurs in the United Kingdom and is typical of the class of 'crêmes,' which are highly sweetened and usually flavoured with only one characteristic ingredient, *e g.* crême d'anis, cacao, café, menthe, noyau, orange, thé, vanille, &c.

The inferior grades are made by flavouring plain spirit with essential oils without distillation whilst the superior qualities are produced by macerating the flavouring ingredients (which sometimes include small quantities of others besides the principal one characteristic of the liqueur) with alcohol and subsequent distillation, sweetening, and colouring.

The following recipe for Crême de Menthe is given by De Brevans (The Manufacture of Liquors and Preserves, New York, 1893): Peppermint, 600 grams; balm, 40 grams; cinnamon, 20 grams; sage, 10 grams; orris root, 10 grams; ginger, 15 grams. These are distilled with 5 litres of alcohol at 85°, the distillate sweetened with 3·75 kilos. of white sugar, and made up to 10 litres.

Curaçoa, so called from the principal island of the Dutch West Indies where the peculiar oranges used for the manufacture of this liqueur, and known as 'Curaçoa apples,' are obtained. These are used before ripening and are exceedingly bitter.

The liqueur is now made chiefly in Amsterdam. The dried peel is rasped to a finely divided condition, macerated for several days in dilute spirit and distilled. A tincture made from various spices as cinnamon, mace, or cloves is often added to the distillate, which is then sweetened with syrup and coloured as desired with Brazil wood, saffron, or caramel. The flavour is said to be improved by the addition of about 1 p c. of Jamaica rum. The alcoholic strength varies from 50 to 75 p.c. of proof spirit, the average being about 60 p.c. proof or approximately 35 p.c. of alcohol by volume.

The following formula is given by De Brevans: rasped skins of 18 or 20 oranges; cinnamon, 4 grams; mace, 2 grams; alcohol at 85°, 5 litres; white sugar, 1·75 kilos. Macerate for 14 days, distil without rectification, and colour with caramel.

Kirsch (see KIRSCHWASSER).

Kümmel, a liqueur made chiefly in Russia and to some extent in the other countries on the shores of the Baltic. The principal flavouring ingredient is caraway seeds. The inferior grades are, as usual, made from plain spirit and essential oils, and the superior qualities by maceration with spirit followed by distillation.

The following formulæ indicate the quantities necessary to make 20 gallons:—(*a*) inferior quality: 7 gallons of spirits of wine; ¼ lb. essential oil of caraway seed; 7½ drachms of fennel seed oil; 15 drops of bitter almond oil; syrup made with 40 lbs. of sugar in 12 gallons of water. When fined with alum or soda solution, it is ready for use. (*b*) Superior quality: 4 lbs. caraway seeds; ¼ lb. fennel; 2 oz. of Florentine iris root. These are macerated with 10 gallons of spirits of wine and 8 gallons of water, and distilled. The first part of the distillate is set aside because of its rough character, and about 8 gallons are then distilled over for making the fine kummel, the last fraction of 3 or 4 gallons being used for the inferior grades. To the middle fraction a syrup made with 60 lbs. of sugar in 10 gallons of water is added, and the whole well mixed in an open heated vessel. The liquor is then cooled and made up with water to 20 gallons. It may be fined with isinglass and stored to mature and mellow.

The strength of kummel varies considerably, viz. from about 60 to 100 p.c. of proof spirit, the average being 75 p.c. proof equivalent to 43 p.c. of alcohol by volume.

Maraschino. This liqueur was originally made at Zara in Dalmatia from the wild *marasca* cherry. The juice was fermented, distilled, aged for two or three years, and subsequently made into liqueur by diluting with syrup. Such liqueur usually contains 30 p.c. to 41 p.c. alcohol and 26 to 36 p.c. sugar. The maraschino prepared from the marasca cherry has a delicate fragrance, quite different from products prepared in a similar way from other varieties of cherry or other fruits. It contains traces of benzaldehyde and of hydrocyanic acid, but usually no added flavouring matters. Genuine maraschino diluted with water, then saturated with sodium bisulphite and extracted with ether, imparts its original odour to ether. French, Dutch and American maraschinos have generally an entirely different flavour from the Dalmatian product and are made by fermenting other varieties of cherries with or without the addition of other fruits (Riley and Sullivan). Other flavouring ingredients are now commonly used, as cherry leaves, kirschwasser, peach kernels, orris root, raspberries, vanilla, &c.

Imitation maraschino may be made from plain spirit flavoured with bitter almonds, raspberry juice and orange flower water, or with essential oils as neroli, noyau, jasmine, and vanilla.

The strength varies from 55 to 75 p.c. of proof spirit, average 69 p.c. proof or 39 p.c. of absolute alcohol by volume.

Noyau is distilled from brandy macerated with or distilled from bitter almonds, sometimes with the addition of other flavourings as cinnamon, coriander seed, ginger, mace, and nutmeg. The almonds are occasionally replaced by apricot or peach kernels or by oil of bitter almonds or its substitute nitrobenzene. The flavour is due chiefly to the presence of prussic acid and the liquor should therefore be used sparingly. It is frequently coloured pink.

Parfait amour may be made by flavouring spirit with the peel of 4 lemons, 1 drachm of essence of vanilla, and 3 lbs. of sugar to the gallon, colouring with cochineal. The essences of lemon, cloves, and mace are also employed in some varieties of this liqueur. The average strength is 60 p.c. of proof spirit or 34·5 p.c. of alcohol by volume.

Peppermint cordial (known also as 'Eau des Chasseurs' or 'Sportsman's cordial') is prepared from oil of peppermint, plain spirit, and sugar. The following is a recipe for making 100 gallons: English oil of peppermint, 5 oz., is added to 3 pints of rectified spirits of wine, well shaken, and placed in a cask capable of holding 100 gallons. 36 gallons of perfectly colourless and flavourless spirit at proof strength are poured in, and the whole well shaken for 10 minutes. A solution of pure sugar, 2¾ cwt. in about 35 gallons of pure soft water (preferably filtered rain water) is added, and the contents of the cask well rummaged for 15 minutes. Sufficient water to make the quantity up to 100 gallons, and containing 5 oz. of alum in solution is next added, and the whole again well agitated for a quarter of an hour. The cask is then bunged down and allowed to rest for a fortnight.

On a small scale, peppermint cordial may be prepared by taking a pint each of peppermint water and gin or plain spirit of about 20 u.p. and adding ¾ lb. of sugar. Peppermint water is prepared by macerating peppermint flowers in about 4 times their weight of water containing about 5 p.c. of salt.

Ratafia. This term is applied to liqueurs or cordials the basis of which is the juice of fruits, obtained either by maceration or simple pressure. One of the most important is Ratafia de Cassis, made from black currants, but other pulpy fruits, especially apricots, cherries, gooseberries, oranges, peaches, raspberries, and strawberries are also commonly used. Various other flavourings as spices, ginger, orris root, &c., are occasionally added to give variety of flavour. The following formula for the preparation of cherry ratafia may be taken as typical: 20 litres of cherry juice; 20 litres of alcohol at 85°; 13·5 kilos. of sugar, and 4 to 8 litres of bitter almond water.

Trappistine. Originally prepared at one of the Trappist monasteries in Italy. Recipe: large absinthe, 20 grams; angelica, 40 grams; mint, 80 grams, cardamom, 40 grams; balm, 30 grams; myrrh, 20 grams; calamus, 20 grams; cinnamon, 4 grams; cloves, 4 grams; mace, 2 grams; alcohol at 85°, 4·5 litres; white sugar, 3·75 kilos. The method of preparation is similar to that described for Chartreuse (*v.* vol. I.). After macerating for 2 days, distil and rectify. Add syrup and colour green or yellow.

Vermouth. The principal varieties of vermouth are the French and Italian, the basis in each case being white wine flavoured with various herbs. Inferior kinds are made from brandy or other spirit sweetened and flavoured with essential oils. The French variety is less sweet and stronger in bitter principles, particularly wormwood, than the Italian.

The following recipe by Ollivero may be used for Italian vermouth: 100 litres of white wine of Picardy; coriander, 500 grams; rinds of bitter oranges, 250 grams; orris root, powdered, 250 grams; elder flowers, 200 grams; red cinchona, 150 grams; calamus, 150 grams; 125 grams each of large absinth, holy thistle, (*Carduus benedictus*), elecampane (roots), little centaury, and germander; Chinese cinnamon, 100 grams; angelica root, 65 grams; 50 grams each of cloves, galanga, and nutmegs; and 30 grams of cassia. Digest for 5 or 6 days, draw off the liquor, size with fish glue and allow to stand for 15 days.

—	Specific gravity	Alcohol by volume	Alcohol by weight	Extract	Cane sugar	Other extractives	Ash
Absinth .	0·9116	58·9	—	0·18	—	0·32	—
Anisette de Bordeaux .	1·0847	42·0	30·7	34·82	37·44	0·38	0·040
Bénédictine	1·0709	52·0	38·5	36·00	32·57	3·43	0·043
Chartreuse .	1·0799	43·2	—	36·11	34·35	1·76	—
Creme de Menthe .	1·0447	48·0	36·5	28·28	27·63	0·65	0·068
Curaçoa .	1·0300	55·0	42·5	28·60	28·50	0·10	0·040
Ginger . .	1·0481	47·5	36·0	27·79	25·92	1·87	0·141
Kummel .	1·0830	33·9	24·8	32·02	31·18	0·84	0·058

The strength of vermouth is usually between 23 and 30 p.c. of proof spirit, the average being 27 p.c. or 15·5° of alcohol by volume.

The above table, by Konig, shows the results of analysis of some of the best known liqueurs and cordials.

J. C.

LIQUEUR DE FERRAILLE. *Ferric acetate* v. ACETIC ACID.

LIQUID STORAX v. BALSAMS.

LIQUORICE. The root of *Glycyrrhiza glabra* (Linn.). Cultivated chiefly in Spain, Russia, Italy, and to a small extent in Germany and England. It requires deep, fertile soil. Wild plants supply a considerable quantity in Asia Minor, and in some portions of Russia. The Spanish product is generally preferred to the Russian, since the latter is somewhat bitter.

The following analyses are given by König—

	Water	Protein	Fat	Glucose	Sucrose	Other N-free extract	Fibre	Ash
Spanish liquorice	8·8	12·9	3·7	7·4	2·1	43·0	17·7	4·4
Russian ,,	8.7	9·3	3·1	6·0	10·1	38·4	18·8	5·4

Liquorice owes its characteristic sweet taste to the presence of *glycyrrhizin* (the calcium and potassium salts of glycyrrhizic acid) which is present to the extent of about 8 p.c. To extract this, the roots are treated with cold water, the liquid boiled to precipitate albuminoids, filtered, and dilute sulphuric acid added, when the glycyrrhizic acid is precipitated in pale yellow flocks, which soon become a dark brown, sticky mass. This is then washed until free from acid and dissolved in dilute ammonia. By evaporation to dryness of this liquid, the "glycyrrhinum ammoniacale" is obtained, which serves as a sweetening agent in the preparation of medicines, in porter-brewing, and also as a sweetmeat.

Liquorice also contains a yellow colouring matter, and from 2 to 4 p.c. of asparagin, malic acid, starch, a little tannin, sucrose, saponins, glycyrrhetic acid, &c. (*cf.* Housemann, Amer. J. Pharm. 1916, 88, 97.

Estimation of Glycyrrhizin in Liquorice Root.—The root is ground to pass a twenty-mesh sieve, and dried at 50°C. to a moisture content of less than 2 p.c. Three grams of the powder are treated in an extraction apparatus with 50 c.c. of ether, dried and transferred to a 100 c.c. centrifuging tube to which 75 c.c. of 75 p.c. alcohol are added. After frequent stirring, followed by standing overnight, the tube is centrifuged, the clear liquid is poured off, and the alcoholic extraction of the residue twice repeated. The mixed extracts are evaporated to dryness, dissolved in 10 c.c. of water, filtered, diluted to 20 c.c., and precipitated by the addition of 3 c.c. of 10 p.c. sulphuric acid. The residue is washed with two 5 c.c. portions of ice-cold water saturated with ether, and dissolved in 30 c.c. of warm 95 p.c. alcohol. The acid solution and washings are mixed and neutralised by the addition of ammonia, evaporated to about 5 c.c. and treated with 2 c.c. of 10 p.c. sulphuric acid, and the precipitate washed with iced ether-water as above. This precipitate is dissolved in 10 c.c. of warm 95 p.c. alcohol, filtered and added to the alcoholic solution of the first residue. To the mixed solutions two drops of 5 p.c. ammonia are added, the solution evaporated to dryness, and the residue dried at 100°C. and weighed. The method yields results considerably higher than do previous methods, and the glycyrrhizin obtained is light in colour, intensely sweet, and free from resins and bitter substances (Housemann, Amer. J. Pharm. 1921, 481–495).

H. I.

LIQUORICE ROOT. (*Glycyrrhizæ Radix.* B.P.; *Glycyrrhiza*, U.S.P. (*Réglisse*, Fr.; *Süssholzwurzel*, Ger.). The peeled root of the underground stems of the *Glycyrrhiza glabra* (Linn.), a plant inhabiting the south of Europe and Central Asia (*cf.* Bentl. a. Trim. 74). Liquorice, or its solid aqueous extract, the 'Spanish juice' of commerce, has long been a favourite demulcent in throat affections, and is used as a laxative. It finds also a considerable employment in porter-brewing. The U.S.P. admits in addition Russian liquorice from *G. glabra glandulifera* (Regel et Herder).

The root was examined chemically many times since 1808; for an exhaustive bibliography, *see* Linz (Arch. Pharm. 1916, 254, 216). It was found to contain *glycyrrhizin* or *liquorice sugar*, the most important constituent, together with an *acrid oil*, *asparagin*, *malic acid*, *starch*, traces of *tannin*, and other substances common to plants.

Glycyrrhizin has been further studied more recently by Tschirch and Cederberg (Arch. Pharm. 1907, 245, 97) and Tschirch and Gauchmann (*ibid.* 1908, 246, 545; 1909, 247, 121). It consists of the potassium and calcium salts of a tribasic crystalline acid, *glycyrrhizic acid* $C_{44}H_{64}O_{19}$ ($C_{44}H_{60}O_{18}$ according to Rasenack, Arb. Reichsgesundh. Amt. 1908, 28). Glycyrrhizic acid melts at 205°, it has a sweet taste and is optically inactive. A hexa-acetyl derivative has been obtained, m.p. 210°. Glycyrrhizic acid does not reduce ammoniacal silver solution or Barreswil's (Fehling's) solution. When fused with potash it yields acetic and oxalic acids; distilled with zinc dust, naphthalene; and when oxidised with potassium permanganate, phthalic acid. If glycyrrhizic acid is boiled for 5 hours with water containing 3 p.c. of sulphuric acid, air being excluded, *glycyrrhetic acid* $C_{32}H_{48}O_7$ (hitherto known as *glycyrrhetin*) is precipitated.

It can be obtained crystalline from acetic acid, melts at 210°, is monobasic, and forms a diacetyl derivative melting at 219°. The solution from which this acid has separated contains glycuronic acid, and the hydrolysis is expressed by the equation:

$$C_{44}H_{64}O_{19}+2H_2O=C_{32}H_{48}O_7+2C_6H_{10}O_7$$

Glycyrrhizic acid contains 6 hydroxyl- and 3 carboxyl-groups; the acid potassium and ammonium salts crystallise well. The former, $C_{44}H_{63}O_{19}K$, is one of the sweetest of vegetable substances; the taste is still perceptible at 1 : 20,000.

The drug contains about 6–7 p.c. of glycyrrhizic acid. Mannitol is present in the liquid from which the crude glycyrrhizic acid has been precipitated with sulphuric acid, but it is not present in the original drug.

By distilling Spanish liquorice root, Haensel (Pharm. Centh. 40, 533) obtained 0·03 p.c. of an ethereal oil, the Russian roots yield 0·035 p.c. These oils are not identical, for whilst the Russian oil is dextrorotatory, the Spanish is lævorotatory.

Linz (Arch. Pharm. 1916, 254, 65, 81, 204) has given an elaborate review of 27 methods for determining glycyrrhizic acid in 'Spanish juice' and liquorice root. The best seems that of Parry (Chemist and Druggist, 1910, 26), which was followed in principle by Housemann (Amer. J. Pharm. 1912, 84, 531) and by Linz.

Russian and Persian liquorice root from *G. glandulifera*, W. and K., contains in addition an amorphous bitter substance. Glycyrrhizic acid is also present in the roots of *Polypodium vulgare*, *P. pennatifidum*, *Periandra mediterranea*, in the shoots of *Myrrhis odorata*, in the bark of *Chrysophyllum glycyphlœum*, and possibly in other plants.

Few words have suffered so many distortions as liquorice. The original Greco Latin *glycyrrhiza*, literally sweet-root, was corrupted into Latin *liquiritia*, whence French *réglisse*, Italian *legorizia*, *regolizia*, and German *Lokritze*. The mid-English form *licoris* would appear to have been influenced by *Orris*, a plant which also had a sweet root, while the modern spelling is perhaps due to *liquor* (Weekley, The Romance of Words).

G. B

LITCHI NUT. The Chinese hazel nut (*Litchi chinensis*, Sonner) occurs in the tropical countries of the East where it is cultivated for medicinal and edible purposes. Contains ash 1·5, protein 2·9, ether extract 0·2, fibre and nitrogen-free extract 77·5, water 17·5 p.c. The alcoholic extract has a cupric reducing power equivalent to 53 p.c. invert sugar, crude fibre 0·4 p.c. Total acidity 0·25 p.c. citric acid (Read, J. Amer. Chem. Soc 1918, 40, 817).

LITHARGE *v.* LEAD.

LITHARGITE and **MASSICOTITE.** Mineralogical terms for the native forms of the well-known substances litharge and massicot, which were formerly included together under the one name (litharge or massicot, or sometimes lead-ochre or plumbic-ochre). Lead monoxide PbO is dimorphous, existing as a yellow orthorhombic (pseudo-cubic) modification with sp.gr. 9·29, mean refractive index β 2·61, optically biaxial and positive; and as a red tetragonal modification with sp.gr. 9·125, ω 2·64, optically uniaxial and negative. They have, however, not been obtained in sufficiently good crystals for an exact determination of their characters, and there is some confusion in the optical descriptions (A. Scott, Min. Mag. 1914, 17, 143). E. S. Larsen and E. T. Wherry (Amer. Min. 1917, 2, 18) propose to restrict the name litharge or lithargite to the yellow orthorhombic modification, and massicot or massicotite to the red tetragonal modification. Larsen describes minute brownish-red scales from California and some other localities as being built up of the two minerals—the central portion of the plates consisting of lithargite and the borders of massicotite, the latter being probably an inversion product of the former. As a fine scaly or earthy encrustation one or other of these modifications is not uncommon as an alteration product of lead ores, though generally in small amounts. In particular, it has been recorded from several localities in Mexico, occurring sometimes as a volcanic product; and in certain streams it has been collected in considerable quantities.

L. J. S.

LITHIA MICA *v.* LITHIUM.

LITHIUM. Sym Li. At.w. 6·94 (Hagen, Mallet, Troost, Diehl, Stas, Dittmar, Richards and Willard) This metal occurs in combination with silica, alumina, and the alkali metals in *lepidolite* or *lithia mica*, *petalite* (containing phosphates of lithium, iron, and manganese), *spodumene*, *triphylene*, and *amblygonite*, usually to the extent of 3 to 6 p.c. (J. Soc Chem. Ind. 18, 877). Also in psilomelane, in a hexagonal variety of zinc sulphide, schalenblende, and in many radioactive minerals particularly carnotite (Gleditsch, Compt. rend. 145, 1148; 146, 331); Ramsay, *ibid.* 146, 456; McCoy, Nature, 1907, 79).

Lithium is widely distributed. It occurs as chloride in most spring waters and in sea water. A mineral spring at Wheal Clifford, near Redruth, contains 26 grains per gallon (Miller, Brit. Assoc. Trans. 1864, 35); Phillips has found 34 grains per gallon in a salt spring in Huel Seton copper mines in Cornwall. It is found in most plants, especially in the leaves (Tschermak, Chem. Zentr. 1899, ii. 1127). The ash of tobacco has been found to contain 0·44 p.c. of lithium chloride (Fruchot, Compt. rend. 78, 1022). The presence of lithium in excess appears to be generally injurious to plants. It also occurs in all the organs of the human body, particularly the lungs (Herrmann, Pflügers Archiv. 109, 26).

Lithium was first isolated by Brandes, but first prepared in quantity by Bunsen (Pogg. Ann. 94, 107). The metal cannot be obtained by ignition of the carbonate with carbon, or of the hydroxide with iron, but is obtained by the electrolysis of a mixture of equal weights of lithium and potassium chlorides (Guntz, Compt. rend. 117, 732). Ruff and Johannsen (Zeitsch. Elektrochem. 12, 186) recommend a mixture of lithium bromide with 10–15 p.c. lithium chloride, using a carbon anode and two iron rods, 4 mm. diameter, as cathode, the current required being 100 ampères and 10 volts. According to Borschers (Chem. Zentr. 1895, ii. 13), lithium can be obtained from its ores by making the solution of the chlorides of the alkalis and alkaline earths slightly alkaline, evaporating in an iron vessel, fusing the residue thus obtained with ammonium chloride and electrolysing the mass with a current of 1000 ampères per square metre of cathode surface and 5 volts. The upper rim of the iron crucible is kept cool by a current of cold water, the surface thus being protected from the atmosphere by a thin layer of solidified metal. The metallic globules are then placed in a paraffin bath at 130°–200° when the pure metal rises to the surface. Lithium can also be obtained by heating the hydroxide with magnesium in a tubulated iron retort when the metal distils over (Warren, Chem. News, 1896, 6); or by the electrolysis of lithium chloride in pyridine solution (Kahlenberg, J. Phys. Chem. 1899, 3602). The metal is also deposited electrolytically from other organic solvents of its chloride (Patten and Mott, J. Phys. Chem. 1904, 8, 153).

Lithium is a mixture of two isotopes of masses 6 and 7 (Aston).

The statement that traces of lithium are formed in the degradation of copper by radium emanation (Cameron and Ramsay, Chem. Soc. Trans. 1907, 1593) lacks confirmation (Perman, *ibid.* 1908, 1775; Curie and Gleditsch, Compt. rend. 147, 345).

Properties.—Lithium is a silver-white metal which tarnishes and oxidises less rapidly than potassium or sodium. It is softer than lead, but less tenacious. Its sp.gr. is 0·589 to 0·598 (Bunsen), lower than that of any known solid. It melts at 180° (Bunsen), 186° (Kahlbaum, Zeitsch. anorg. Chem. 23, 220), and volatilises at a bright red heat in a current of hydrogen, forming *lithium hydride* LiH (Guntz, Compt. rend. 122, 244). Electrolysis gives lithium as the cathode and apparently hydrogen as the anode, this being the first observed instance of hydrogen functioning as a negatively charged ion. Sp.gr. 0·816. At a temperature somewhat above its melting-point it burns with an intense white light. When heated, it burns in chlorine, bromine, iodine, and sulphur vapour, and in carbon dioxide. In water it oxidises, but does not fuse. It absorbs nitrogen even in the cold, being the only metal that does so (Deslandres, Compt. rend. 121, 886; Guntz, *ibid.* 245) to form *lithium nitride* Li_3N, m.p. 840°–845°, which rapidly attacks iron, nickel, copper, platinum, porcelain and other silicates. When heated in hydrogen to 250° forms *trilithium ammonium* Li_3NH_4 which on further heating to 480° forms *lithamide* (v. *infra*), an extremely hygroscopic substance, evolving hydrogen and ammonia under the action of water (Dafert and Miklauz, Monatsh. 1910, 31, 981; *ibid.* 1912, 33, 63).

By nitric acid it is rapidly oxidised, often with fusion and ignition. In dilute sulphuric acid and in hydrochloric acid it dissolves quickly; solution is slow in strong sulphuric acid. At a temperature below 200° it attacks silica, glass, and porcelain. Like other alkaline metals it dissolves with formation of a blue solution in liquefied ammonia gas, a similar result being obtained when it dissolves in methylamine (Moissan, Compt. rend. 128, 26). When gently heated to 400° in a current of ammonia, *lithamide* $LiNH_2$ is formed (Titherley, Chem. Soc. Trans. 1894, 517; Moissan, Compt. rend. 127, 685; *ibid.* 133, 715; Ruff and Georges, Ber. 1911, 44, 502; Dafert and Miklauz, Ber. 1911, 44, 809).

At the ordinary temperature, lithium with dry ammonia gas forms a liquid which, when rapidly evaporated at 70°, yields a brownish-red solid, *lithium ammonia* $LiNH_3$ (Moissan, *l.c.*).

Lithium forms several amalgams with mercury (Kerp and Böttger, Zeitsch. anorg. Chem. 25, 1; Schukoffsky, *ibid.* 1911, 71, 403) and alloys with antimony, tin, and lead of the type Li_3M (Lebeau, Compt. rend. 130, 502; *ibid.* 134, 231, 284). These alloys have higher melting-points than the constituents and are powerful reducing agents. It also forms compounds with arsenic (Lebeau, *ibid.* 129, 47) and with silicon (Moissan, *ibid.* 134, 1083; Wallace, Zeitsch. anorg. Chem. 63, 1).

Detection.—Lithium salts produce a fine, crimson colour in the blowpipe flame. They are usually colourless, and when in strong solution give a precipitate on addition of carbonates or sodium phosphate, in presence of ammonia. In presence of sodium, lithium can be detected by making the solution alkaline with ammonia, then adding $\frac{1}{10}$ of its volume of sodium hydrogen phosphate, after which enough alcohol is added to produce a heavy permanent precipitate. On boiling, the solution will become perfectly clear if lithium is absent, for lithium phosphate is insoluble in boiling alcohol (Benedict, Amer. Chem. J. 32, 480).

For its *absorption spectrum*, *see* Bevan, Proc. Roy. Soc. 1911, 85, A, 54.

Estimation.—The estimation usually entails the separation from potassium and sodium. For this separation Mayer's process is most satisfactory (Annalen, 98, 193). The solution containing the alkalis as chlorides is treated with sodium phosphate (*absolutely* free from alkaline earth phosphates), and sufficient sodium hydroxide to keep the solution alkaline, and evaporated to dryness. Sufficient water is added to dissolve the soluble salts, the solution heated gently and filtered after 12 hours. The precipitate is washed with a mixture of 1 part of water and 1 part of ammonia (of which liquid 3920 parts dissolve only 1 part of lithium phosphate); the filtrate and first two washings are evaporated and taken up as before, any residue of lithium phosphate being added to the bulk of precipitate. The precipitate, dried at 100°, has the composition Li_3PO_4.

Kahlenberg and Krankopf (Amer. Chem. J. 30, 1104) recommend the following method. The solution of mixed chlorides is evaporated to dryness and the residue is boiled with pyridine. The solution is decanted through a small filter and the residue is again treated with pyridine several times. The pyridine filtrates are now distilled and the lithium chloride residue is converted into sulphate by evaporation with sulphuric acid and weighed as such. According to Schieffelin and Lamar (Amer. Chem. J. 24, 392) a good way of estimating lithia in lepidolite is to dissolve the alkali chlorides obtained in the usual way in about 10 c.c. of hot water, a drop of hydrochloric acid is added, then a little ammonia and ammonium oxalate; the solution is filtered and the filtrate evaporated until it commences to crystallise (about 1–2 c.c.). A drop of water and of hydrochloric acid is added, then 15 c.c. of amyl alcohol, it is then concentrated to half its volume, cooled and filtered into a platinum dish, the residue is washed with amyl alcohol until the washings are free from lithium, the amyl alcohol extract is evaporated below the boiling-point and the residue converted to sulphate.

For methods of estimating lithium in mineral waters, compare Carnot (Compt. rend 107, 336); Waller (J. Soc. Chem. Ind. 1890, 1066); Razoli (Gazz. chim. ital. 31, i. 40).

Extraction of salts.—Finely powdered lepidolite or petalite 10 parts, is mixed with barium carbonate 10, barium sulphate 5, potassium sulphate 3, and ignited at the highest temperature of a wind furnace. Two layers are thus produced, the lower of barium silicate and sulphate, the upper of white sulphate of potassium and lithium. It is lixiviated with water and treated with barium chloride to convert the alkalis into chlorides and to precipitate the sulphuric acid as barium sulphate The solution is evaporated to dryness and digested with a mixture of equal parts of absolute alcohol and ether, in which the lithium chloride dissolves with only a trace of potassium and sodium chloride (Troost, Compt. rend. 43, 921).

According to Muller (Annalen, 85, 251), *triphyline* is dissolved in hydrochloric acid, the iron oxidised to ferric chloride by the addition of nitric acid, the phosphoric acid precipitated by a persalt of iron, the mixture evaporated to dryness, and extracted with water. Manganous and lithium chlorides are thus dissolved; the former is precipitated with barium sulphide, the excess of barium being removed by the addition of ammonium carbonate or sulphuric acid. The solution is evaporated with oxalic acid and the residual oxalate ignited to carbonate.

The finely ground and sifted lepidolite is made into a thin paste with concentrated sulphuric acid, in a warm brick trough, and digested and stirred until it commences to agglomerate. It is then calcined in a reverberatory furnace, and, while warm, well lixiviated with water and filtered. The lye is mixed with sufficient potassium sulphate to convert all the alumina into alum, and the solution decanted from the alum meal. The remaining alumina is precipitated by milk of lime, the alkalis are converted into chlorides by addition of barium chloride, and the solution evaporated to dryness. The chlorides of lithium and calcium are extracted with absolute alcohol, the alcohol evaporated, and the calcium precipitated by ammonium oxalate, and any heavy metals removed by a little ammonium sulphide. The solution is evaporated to dryness in a silver basin (*v.* A. W. Hofmann, Dingl. poly. J. 219, 183, and Felsinger, *ibid.* 222, 385).

Powdered amblygonite or other lithium ore is intimately mixed with powdered sodium bisulphite and the mixture heated in cast-iron retorts, the hydrofluoric acid and silicon fluoride disengaged being collected. The mass is then transferred to a refractory earthen vessel and heated to redness. The product is lixiviated, filtered, and aluminium, copper, and iron are precipitated by a very small proportion of sodium carbonate. After filtration it is again treated with sodium carbonate when lithium carbonate is precipitated. The insoluble residue of the lixiviated product is said to be rich in phosphorus and can be used as a manure (J. Soc. Chem. Ind. 1906, 884).

Finely powdered lepidolite is mixed with 10 p.c. more than its weight of sulphuric acid and heated with frequent stirring for 8 hours at 112°–340°; 97 99 p.c. of the ore is thus decomposed. The mass is leached with water and the silica separated. The solution is now treated with sufficient potassium sulphate to convert the aluminium sulphate to alum and allowed to stand for 6 days when precipitation is complete, the decanted liquor is treated with whiting, boiled, and the alum precipitated as alunite by adding aluminium hydroxide. The last traces of alumina are removed by again treating the filtrate with whiting. The solution is then boiled, made alkaline with slaked lime and concentrated. Copper sulphate and magnesium and iron oxides are removed in the usual way and the solution consisting of lithium sulphate is added to a solution of potassium carbonate, when lithium carbonate is precipitated, and is washed and dried (Schieffelin and Cappon, J. Soc. Chem. Ind. 1908, 549).

According to Wadman (*ibid.* 1907, 469; 1908, 122), pure lithium carbonate can be obtained by heating the ore with an alkaline sulphate such as K_2SO_4. The solution of sulphates thus obtained is now treated with sufficient ammonia to render the potassium sulphate insoluble and to precipitate iron, aluminium, and magnesium hydroxides The precipitate is removed and the lithium precipitated as carbonate.

According to Zell (J. Soc. Chem. Ind. 1909, 1126), a pure lithium compound can be obtained by heating a lithium ore in the presence of carbon in an atmosphere of acetylene. Volatile lithium hydrogen carbide is thus formed and is decomposed by water into lithium hydroxide and acetylene.

Lithium oxide Li_2O may be prepared by ignition of the metal in air or oxygen (Holt and Sims, Chem. Soc. Trans 1894, 443); in solution, by precipitation of the sulphate with barium hydroxide solution. A purer product is obtained by heating lithium hydroxide or its hydrate $LiOH$, or $Li(OH)\cdot H_2O$, in a platinum crucible in a current of dry hydrogen for about an hour at 780° (Forcrand, Compt. rend. 144, 1321). Lithium carbonate heated similarly at 780°–800° also yields pure lithium oxide (Forcrand, *l.c.* 1402). It is yellowish white and spongy, less soluble than the oxides of potassium and sodium. It melts at 462°, and, as it corrodes platinum powerfully, should be fused in a silver vessel. The hydrated oxide may be obtained in small crystalline grains. Lithium hydroxide is used in a certain type of storage battery.

By mixing lithium hydroxide (Forcrand, Compt. rend. 146, 802) with hydrogen peroxide and then adding an equivalent volume of absolute alcohol, the compound

$$Li_2O_2\cdot H_2O_2,3H_2O$$

is formed which, when placed in a vacuum over phosphorus pentoxide, yields *lithium peroxide* Li_2O_2 (Forcrand, Compt. rend. 130, 1465). Lithium hydroxide gradually dissolves hydrated silicic acid in the cold. A hot solution forms insoluble *lithium silicate* $Li_2SiO_{31}H_2O$ as a white granular precipitate.

Lithium chloride LiCl may be prepared by combination of lithium and chlorine, or by dissolving the carbonate or oxide in hydrochloric acid. When formed at low temperatures the crystals contain two molecules of water; at temperatures above 15° anhydrous octahedral crystals are produced, which are very hygroscopic; various hydrated chlorides are known (Bogorodsky, Chem. Zentr. 1894, ii. 514). It dissolves in absolute alcohol and in a mixture of alcohol and ether. At 0° 100 parts of water dissolve 63·7 parts, and at 100° 145 parts of the chloride.

Lithium chloride melts at 605° and is more volatile than potassium chloride; less so than sodium chloride. Below a red heat it volatilises, losing a little hydrochloric acid and producing an equivalent amount of lithium oxide.

Lithium chloride is used to some extent in pyrotechny.

Lithium dissolves in the chloride, but the subchloride Li_2Cl could not be obtained (Guntz, Compt. rend. 1895, 121, 945; Ann. Chim. Phys. 1907, 10, 13). At −18° the chloride absorbs ammonia rapidly, forming a series of compounds with 1, 2, 3, and 4 molecules of ammonia (Bonnefoi, Compt. rend. 124, 771; *ibid.* 127, 367). With ethylamine and methylamine, it behaves similarly (Bonnefoi, *l.c.* and Compt. rend. 129, 1257). Lithium bromide (Bonnefoi, *ibid.* 130, 1394; Bogorodsky, *l.c.*), lithium iodide (Thirsoff, J. Russ. Phys. Chem. Soc. 25, 467; Bogorodsky, *l.c.*), and their double salts with other metallic halides (Kurnakoff and Sementschenko, Zeitsch. anal. Chem. 1899, 335; Dobroserdoff, J. Russ. Phys. Chem. Soc. 32, 774; Bogorodsky, *l.c.* 515). Lithium bromide and iodide have been used in photography (Duboin, Compt. rend. 141, 1015; Chassevant, *ibid.* 115, 113); lithium periodate (Barker, Chem. Soc. Trans. 1911, 1326); also lithium fluoride (Poulenc, Bull. Soc. chim. [iii.] 11, 15; Wells and Foote, Amer. J. Sci. 1897, 466) have been prepared. (*Cf.* Scarpa, Atti R. Accad Lincei, 1915, [v.] 24, ii. 476.)

Lithium sulphate Li_2SO_4 is prepared by dissolving the carbonate or oxide in sulphuric acid. It forms monoclinic plates, soluble in alcohol and water. It produces a double sulphate with potassium sulphate, but does not form an acid sulphate or an alum.

Lithium carbonate Li_2CO_3 is prepared by the addition of a hot, concentrated solution of lithium chloride to an ammoniacal solution of ammonium carbonate. It is a white powder, which decomposes at 600° (Lebeau, Compt. rend. 136, 1256), is reduced by heating with aluminium (Franck, Chem. Zeit. 1898, 22, 236), and is more fusible than the potassium and sodium salts It is quite insoluble in absolute alcohol (Kobbe, Pharm. Zeit. 34, 312) and only slightly soluble in water, but more readily so in aqueous solution of the alkalis, particularly ammonium salts (Geffcken, Zeitsch. anorg. Chem. 1905, 43, 197).

Its solubility in cold is greater than in hot water. The solubilities given by different observers are not concordant. According to Bevade (Bull. Soc. chim. [ii.] 43, 123), the solubility in 100 parts of water is as follows:—

Temperature	0°	10°	20°	50°	75°	100°
Parts . .	1·539	1·406	1·329	1·181	0·866	0·728

The solubility increases after continued boiling. *Cf.* further Draper (Chem. News, 55, 169) and Flückiger (Arch. Pharm. [iii.] 25, 509).

The commercial salt usually contains about 98·5 p.c. of lithium carbonate. Lithium forms a very soluble *urate*: for this reason the carbonate and citrate are administered to remove uric acid from the blood in gouty affections (Kebler, Amer. J. Pharm. 1898, 600).

Lithium carbonate mixed with carmine is used as a nuclear stain.

Lithium carbide Li_2C_2, is obtained by heating lithium carbonate with sugar carbon in an electric furnace (Moissan, Compt. rend. 122, 362); or by heating lithium and carbon together in a vacuum (Guntz, *ibid.* 126, 1866); or in a stream of carbon di- or monoxide (Guntz, *ibid.* 123, 1273; Moissan, *ibid.* 127, 911). It is a powerful reducing agent; burns in fluorine, chlorine, bromine, iodine, oxygen, and combines with sulphur and selenium; it is not attacked by concentrated acids but readily by water, forming acetylene and lithium oxide.

Lithium nitride Li_3N is prepared by heating lithium in an iron dish very gently in a slow stream of nitrogen (Ouvrard, Compt. rend. 1892, 114, 120; Guntz, *ibid.* 123, 995). It is a brownish-red or black spongy substance, difficult to obtain quite pure and is readily decomposed by water or when heated with hydrogen.

Lithium cyanide is used in X-ray work.

Lithium azoimide LiN_3,H_2O, formed by neutralising a solution of lithium hydroxide with azoimide, HN_3, crystallises in colourless, lustrous, hygroscopic needles which explode between 115°–298° (Dennis and Benedict, Zeitsch. anorg. Chem 1898, 17 18; Curtius and Rissow, J. pr. Chem. 1898 [ii.] 58, 261).

Lithium citrate $Li_3C_6H_3O_7$ is prepared by the addition of 100 parts of lithium carbonate to a solution of 186·5 parts of citric acid (Umney, Year-book of Pharmacy, 1875, 559). It may be produced as a white, anhydrous, neutral, non-deliquescent powder, or in crystals containing 4 molecules of water. It is soluble in 25 parts of cold water. The commercial salt usually contains salts of potassium, sodium, and calcium, and frequently lithium carbonate or citric acid, and powdered lepidolite or petalite (C Thompson, Pharm. J. [iii.] 13, 783; Dott, *ibid.* 1905, 440). The following salts of lithium are employed in medicine:—

Benzoate, caffeine sulphonate, dithiosalicylate, formate, guaiacate, hippurate, and iodate in uric acid diathesis; bitartrate, theobromine salicylate, potassium tartrate and acetate as diuretics; glycerophosphate in neurosthenia; borosulphite, sulphoichthyolate, and sozoiodolate as antiseptics (J. Soc. Chem. Ind. 1898, 736; Kebler, Amer. J. Pharm. 1899, 57).

According to Vulpian (J. Soc. Chem. Ind. 1889, 476) lithium salicylate is of greater effect than sodium salicylate in gout and in acute articular rheumatism.

Lithium quinate is used in the treatment of gout and analogous diseases (Johnson, J. Soc. Chem. Ind. 1899, 1051). According to Dumesnil (J. Pharm. Chim. 1906, 326), lithium theobromine, prepared by adding excess of theobromine to lithium hydroxide solution, is 4 or 5 times as active therapeutically as the same weight of theobromine.

Coal tar products have largely superseded lithium salts in the treatment of rheumatism and allied affections.

Lithium salts react with casein giving readily digestible compounds suitable for medical purposes (Abel, J. Soc. Chem. Ind. 1899, 398).

Lithium oxalate (Foote and Andrew, Amer. Chem. J. 1905, 153), thymate (J. Soc. Chem. Ind. 1906, 714), and the double salts of lithium and the acid salts of piperazine with oxalic, tartaric, and citric acids (*ibid.* 1897, 758), are also very useful products.

Double urinates (Melikoff and Pissarjewsky, Ber. 30, 2902; Coninck and Chauvenet, Bull. Belg. Roy. Acad. 1905, 51, 182); lithium phosphates and arsenates (Schulten, Bull. Soc. chim. [iii.] 1, 479; Ouvrard, Compt. rend. 110, 1333; Rammelsberg, Chem. Zentr. 1891, ii. 790; Quartaroli, Gazz. chim. ital. 1907, i. 598); zirconates (Ouvrard, Compt. rend. 112, 1444; Venable and Clarke, Amer. Chem. J. 1896, 434); borates (Reischle, Zeitsch. anorg. Chem. 4, 169; Chatelier, Compt. rend 124, 109); alumino-silicates (Weyberg, Centr. Min. 1905, 646); platinocyanides (Reynolds, Proc. Roy. Soc. 1909, 82, 380), and tungstates (Feist, Ber. 21, 133) have been prepared. Lithium tungsten bronze, LiW_5O_{15} (Hallopeau, Compt. rend. 127, 512) is prepared by the electrolysis of lithium para-tungstate.

LITHIUM-DIURETIN. Trade name for a combination of theobromine-lithium and lithium salicylate.

LITHOFELLIC ACID $C_{24}H_{42}O_5$ occurs in the stones of intestinal origin found in the Benzoar-goat, llama, and other cattle; it is probably formed by reduction of cholic acid (Fischer, Ber. 1914, 2728).

Preparation.- The stone is dissolved in methyl alcohol and the acids precipitated by the addition of light petroleum. These are dissolved in alkali and any lithobilic acid is thrown down by the addition of barium chloride. On acidifying the filtrate with hydrochloric acid, lithofellic acid is precipitated and is recrystallised from alcohol (Junger and Klages, Ber 1895, 3045), or ethyl acetate (Fischer, *loc. cit.*)

Properties.—M.p. 205° (corr.). Crystallises from dilute alcohol with 1 mol. H_2O. Insoluble in water, sparingly soluble in ether; $[\alpha]_D^{20}=13{\cdot}1$. On boiling with alcohol hydrochloric acid gives a lactone, b.p. 245°–248°/16 mm. I. S. M.

LITHOFRACTEUR *v.* EXPLOSIVES.

LITHOGRAPHIC STONE. A fine-grained limestone of uniform texture, breaking with an imperfect conchoidal fracture, and free from spots and veins. It must be compact enough to take a good polish and yet sufficiently porous to absorb the grease of the draughtsman's crayon; whilst being a limestone it can be etched with cold dilute acid. The only stones possessing these properties in a high degree are those from the large quarries at Solenhofen and Pappenheim in central Bavaria. Here the rock is a thin-bedded limestone of Upper Jurassic age. Two qualities are distinguished—a yellowish-drab and a bluish-grey, the latter being rather harder and more serviceable. They consist of 81–96 p.c. $CaCO_3$, 1–18 p.c. $MgCO_3$, with small amounts of alumina, ferric oxide, silica, &c. The quality of the stone depends, however, on physical characters rather than on chemical composition. Many attempts have been made to find lithographic stone at other localities, more particularly in the United States, the most promising being at Brandenburg in Meade Co., Kentucky (*v.* G. P. Merrill, The Non-metallic Minerals, 2nd edit., New York, 1910). L. J. S.

LITHOMARGE. (*Steinmark*, Ger.). An amorphous substance, resembling clay (kaolinite and halloysite) in composition (hydrated aluminium silicate with some iron) and in most of its physical properties, but firmer and more compact. It occurs on a large scale in the basaltic lavas of Antrim, where it is associated with bole, bauxite, and aluminous iron-ore. Some of the Irish lithomarge is of lavender colour, with white specks of bauxite, whilst other varieties are brown or blackish. The substance is known to the workmen as 'marge.' It may have resulted from the alteration of the basalt, and appears to resemble some of the steatitic laterites of India. Where peaty water comes in contact with the lithomarge, it occasionally deposits manganese oxide in considerable quantity (*v.* P. Argall, Journ. Geol. Soc. Ireland, 1886, 16, 102; G. H. Kinahan, *ibid.* 307). The following analyses, I–III, by D. Jardin, of lithomarge from Co. Antrim are quoted from G. A. J. Cole, The Interbasaltic Rocks (iron ores and bauxites) of North-east Ireland, Mem. Geol. Surv. Ireland, 1912. IV is of lithomarge from Cook's Kitchen mine, Cornwall:

	I.	II.	III.	IV.
SiO_2 . .	31·70	41·14	39·17	48·3
TiO_2 .	4·68	1·80	3·40	—
Al_2O_3 . .	25·99	27·96	28·41	36·4
Fe_2O_3 . .	19·89	1·92	2·67	—
CaO . .	0·67	1·66	0·70	—
MgO . .		0·77	0·02	—
H_2O . .	12·70	13·94	12·56	14·5
H_2O (at 110°)	4·18	8·26	13·32	
	99·81	100·45	100·25	99·2

Lithomarge occurs in several Cornish mines; a fine yellowish variety, with purple veins, being found at Cook's Kitchen, near Redruth. Closely allied to lithomarge is the *teratolite* of Saxony, formerly reputed to possess such powerful medicinal qualities that it was described by old writers as *terra miraculosa Saxoniæ*.

L. J. S.

LITHOPONE. A pigment prepared by strongly heating a mixture of zinc sulphide and barium sulphate, obtained by mixing solutions of barium sulphide and zinc sulphate. Is a variable mixture of zinc oxide, zinc carbonate, zinc sulphide, normal and basic zinc sulphate, barium sulphate and carbonate, with traces of ferric oxide, alumina, lime, and magnesia. The usual process of manufacture is to heat heavy spar with carbon, dissolve the mass in water and mix with a solution of zinc vitriol. The precipitate is washed, dried, and ignited, mixed with 2–3 p.c. of sal ammoniac and again ignited. While hot it is thrown into water, dried, and finely ground. Its value depends upon the amount of zinc sulphide present. For methods of analysis *v.* J. Soc. Chem. Ind. 1902, 1145; Austin and Keane, Analyst, 1912, 37, 238. The following analyses of different samples are by Austin and Keane (*loc. cit.*):

	I. (German)	II. (English)	III.
$BaSO_4$ . . .	64·36	67·59	72·80
ZnS . . .	30·98	27·82	24·14
ZnO . . .	0·55	1·82	0·88
CaO, F_2O_3, $BaCO_3$, &c.	4·11	2·77	2·18
	100·00	100·00	100·00

Inferior qualities sometimes contain natural barytes which reduce the opacity and covering power and cause it to give a yellowish white tint when used in linoleum. The natural mineral may be detected by means of the microscope, the precipitated sulphate appearing as a fine powder composed of minute crystals of uniform size whereas the natural barytes consists of transparent irregular fragments of larger size (Stewart, J. Soc. Chem. Ind. 1920, 39, 188T.). For conditions determining the resistance of lithopone to change in sunlight in presence of moisture, due, it is surmised, to a dissociation of the illuminated surface with liberation of metallic zinc of a grey colour, see Steinau, Chem. Zeit. 1921, 45, 741.

LITMUS. *Tournesol en pain.* This colouring matter is well known to the chemist, since white paper impregnated with its solution in a slightly acid or alkaline condition has long been employed, under the name of red and blue litmus-paper, to indicate the presence, in any solution, of alkalis or acids respectively. Alkalis change the colour of red litmus-paper to blue, acids turn blue litmus-paper red. In alkalimetry litmus tincture was formerly the most generally adopted indicator. This use depends upon the fact that the free colouring matter of litmus is red, whereas its alkali salts are blue.

Commercial litmus has the form of small pale blue cubes, composed essentially of gypsum and chalk mixed with but comparatively little colouring matter, which is largely present in the form of a lake.

It is said to be prepared, chiefly in Holland, from various species of lichens, *e.g. Lecanora tartarea, Roccella tinctoria*, &c., the same, indeed, as are used in the manufacture of orchil (*q.v.*). Under the combined influence of ammonia and atmospheric oxygen the proximate principles contained in these lichens yield *orceïn*, the alkali salts of which are purple (orchil); but if potassium or sodium carbonate is present at the same time, the reaction proceeds further, and ultimately *azolitmin* (the colouring matter of litmus), the alkali salts of which are blue, is produced.

According to Gélis (J. Pharm. Chim. 24, 277; Revue Scient. 6, 50), litmus may be prepared as follows. Orchil-weed is ground and mixed with half its weight of potassium carbonate, and then repeatedly moistened with urine saturated with ammonium carbonate or with an aqueous solution of this salt; the mass soon acquires a brownish-red colour (3 days), which gradually becomes purple (20–25 days), and finally blue (30 days), yielding a litmus of the best quality in 40 days. The pulpy mass is mixed with chalk and gypsum, then moulded in the form of cubes, and dried in the shade.

By modifying the action of air and ammonia upon orcinol, through the addition of sodium carbonate, De Luynes also succeeded in obtaining the colouring matter of litmus (Compt. rend. 59, 49; Dingl. poly. J. 174, 61; Chem. Zentr. 1865, 127; J. 1864, 551). A mixture of 1 part orcinol, 25 parts cryst. sodium carbonate, 5 parts water, and 5 parts ammonia solution, was heated to 60°–80° for 4–5 days with frequent agitation. On diluting the blue solution thus obtained and acidifying slightly with hydrochloric acid, the colouring matter was precipitated. On washing and drying, it assumed a metallic lustre. It is sparingly soluble in water, but readily soluble in alcohol and in ether.

In making a litmus solution to be employed as indicator, the commercial litmus is extracted with boiling water, the filtered solution is slightly acidified with acetic acid, then carefully neutralised with ammonia, and boiled to expel any excess of the latter. Kept for any lengthened period in stoppered bottles, the solution becomes decolorised in consequence of a reductive fermentation; on exposure to air, however, the original colour is restored. This defect is prevented by saturating the solution with sodium chloride (Reichelt). Compare also Bellamy, J. Pharm. Chim. [v.] 18, 433.) A dry litmus-extract may be prepared according to Vogel in the following manner (*ibid.* 45, 64, 70; Chem. News, 1864, 205). Twenty grams powdered commercial litmus are twice digested, each time with 150 c.c. cold distilled water. The second solution, which is alone employed, is divided into two equal portions, one of which is slightly acidified with nitric acid and then mixed with the other. The purplish solution thus obtained is evaporated to dryness on the water-bath, and the granular amorphous mass is kept in a stoppered bottle ready for dissolving in water when required.

For the employment and characteristics of litmus as an indicator *v.* R. T. Thomson (J. Soc. Chem. Ind. 6, 198); also art. ACIDIMETRY, vol. i.; Marsh (Chem. News, 61, 2); Berthelot (Ann. Chim. Phys. [vii.] 25, 39); Ronde (Pharm. Zeit. 41, 736); Lescouer (Compt. rend. 123, 811); Luttke (Zeitsch. anal. Chem. 31, 692); Foerster (*ibid.* 28, 428); Glaser (*ibid.* 38, 273).

Litmus exhibits a characteristic absorption spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which absorbs the more refrangible end of the spectrum to a point midway between D and E. If the solution is coloured blue by adding a drop of ammonia, an absorption-band is formed, commencing at D, where it is extremely black, and gradually diminishing to E. A blue aqueous commercial solution shows a well-marked absorption-band at D. Addition of acid changes the colour to red, the band at D disappears, and the spectrum now resembles that of œnolin, the colouring matter of red wine (A. H. Allen, Com. Org. Analysis, 325). (Compare also Vogel, Praktische Spectralanalyse, 1877, 269.)

Our knowledge of the chemistry of the colouring matters contained in litmus is very meagre. Gélis (J. Pharm. Chim. 27, 477) extracted from it several colouring matters in the following manner. After extracting commercial litmus with water, the insoluble residue is boiled with dilute caustic alkali and the filtered solution is precipitated with basic lead acetate. The blue precipitate is washed by decantation until it begins to dissolve and colour the wash-water. It is then decomposed with hydrogen sulphide, exposed to air until free from excess of H_2S, collected on a filter and digested with dilute ammonia to extract the colouring matter. On adding acid to the filtered solution the main portion of the litmus colouring matters is thrown down as a red flocculent precipitate. The filtrate from this contains a very small quantity of colouring matter (α).

On extracting the dried red precipitate with ether and leaving the orange solution to spontaneous evaporation, it yields a bright-red residue (β) containing crystalline needles This product is insoluble in water, but readily soluble in alcohol, also in alkalis with a violet colour. The portion insoluble in ether is dissolved in alcohol, and on allowing the blood-red solution to evaporate spontaneously it yields a large quantity of a reddish-purple product (γ) having a bronze lustre. This represents the colouring matter most abundant in litmus.

The residue, which is insoluble in water, in alcohol, and in ether, contains another product (δ) which is soluble in alkalis, from which it may be precipitated by acids. The three products β, γ, and δ, appear to contain nitrogen.

An examination of litmus was made in 1840 by Kane (Royal Soc. Trans. 1840, 298; Ann. Chim. Phys. [iii.] 2, 129; Annalen, 39, 57; J. Pharm. Chim. 1841, 569), who isolated from it the chief and characteristic colouring matters *azolitmin* and *erythrolitmin*, together with *erythrolein* and *spaniolitmin*.

According to Kane, finely powdered commercial litmus is extracted with boiling water. Most of the colouring matter remains in the form of an insoluble lake in the residue, to which hydrochloric acid is added till effervescence ceases and the mixture is strongly acid. The insoluble matter mixed up with liberated colouring-matter is collected on a filter, washed free from acid, dried, and extracted with boiling alcohol. The alcoholic solution is filtered from an insoluble reddish-brown mass (impure azolitmin) and then evaporated to dryness, and the residue is digested with warm ether until it becomes no longer coloured. On distilling the filtered ethereal solution, *erythrolein* is left as a purple semi-fluid oily substance. That portion of the alcoholic extract which is insoluble in ether consists of *erythrolitmin*.

The above-mentioned impure azolitmin is purified, either by dissolving it in a large quantity of boiling water and evaporating the solution to dryness, or by dissolving it in very dilute ammonia, evaporating the solution to dryness, neutralising any residual ammonia by dilute hydrochloric acid, and washing with alcohol until free from ammonium chloride and excess of hydrochloric acid. The residue represents purified *azolitmin.*

The colouring matter contained in the deeply coloured solution obtained in the first instance by boiling the commercial litmus with water and filtering, is isolated as follows The solution is precipitated with neutral lead acetate, the purple precipitate thus obtained is well washed, suspended in water, and decomposed with hydrogen sulphide. The mixture of lead sulphide and liberated colouring matter thus obtained is well washed and digested with warm dilute ammonia; the filtered deep-blue solution is evaporated to dryness, the residue is moistened with hydrochloric acid, washed free from ammonium chloride and any excess of hydrochloric acid, with warm alcohol. The residual deep brownish-red powder consists usually of nearly pure azolitmin, more rarely of *spaniolitmin*, a substance very similar to azolitmin, but which does not contain nitrogen.

Since spaniolitmin occurs so rarely in litmus, and erythrolein is coloured reddish-purple and not blue by alkalis, Kane considers azolitmin and erythrolitmin to be the essential colouring matters of litmus, in which they are combined with ammonia, potash, and lime, and mixed with a considerable quantity of chalk, gypsum, &c.

Azolitmin is a deep brownish-red amorphous powder, insoluble in alcohol and sparingly soluble in water, but readily soluble in alkaline solutions with a pure blue colour. Its ammoniacal solution gives with metallic salt solutions blue or purple precipitates according as they are more or less basic in character. Kane's formula for it is $C_9H_{10}NO_5$, but Gerhardt considers it is best represented by $C_7H_7NO_4$. It differs from all the other colouring matters isolated from litmus by containing nitrogen. Gerhardt considered it to be derived from orcinol, possibly in accordance with the following equation:

$$C_7H_8O_2+NH_3+3O=C_7H_7NO_4+H_2O$$

or from orcein thus $C_7H_7NO_3+O=C_7H_7NO_4$.

If the percentage composition assigned to this substance is correct, the explanation of the part played by the necessary alkaline carbonate in the manufacture of litmus may be that it facilitates and increases the oxidation of the orcinol, so that the orcein at first formed is changed into azolitmin (Gerhardt, Ch. Org. 3, 816)

Scheitz (Zeitsch. anal. Chem. 1910, 49, 736) has isolated from litmus a blue colouring matter distinct from azolitmin in quantity equivalent to 1·5 p.c of the weight of the purified material. It consists of a bright brown powder soluble in formic acid, pyridine, and ammonia, forming a bluish-violet solution with the last-named solvent. It absorbs ammonia gas with production of a dark blue ammonia compound, which dissolves in water to a reddish solution. This ammonia compound is a more delicate indicator than the corresponding derivative of azolitmin.

Erythrolitmin, which also constitutes one of the most important ingredients of litmus, is a bright-red powder, sparingly soluble in water and in ether. It is abundantly soluble in alcohol, from which it may be crystallised in the form of dark-red granular crystals. In strong caustic potash it dissolves with a blue colour. With ammonia it forms a blue compound which curiously enough is totally insoluble in water. With metallic salts it forms lakes of a fine purple colour. According to Kane its formula is $C_{13}H_{22}O_6$, and he considers it to be an oxidation product of his erythroleic acid ($C_{13}H_{22}O_4$) obtained from orchil.

Erythrolein forms a crimson semi-fluid mass, almost insoluble in water, soluble in ether and in alcohol with a red colour, and in ammonia with a purple colour. With metallic salts it gives purple lakes. Kane gives its formula as $C_{13}H_{22}O_8$. Its general properties are very similar to those of the above-mentioned erythroleïc acid.

Spaniolitmin occurs but rarely in litmus, hence its name. It is a bright-red substance, insoluble in alcohol and in ether, and very sparingly soluble in water. It dissolves in alkalis with a blue colour and gives lakes very similar to those of azolitmin. Kane's formula for it is $C_9H_7O_8$.

Under the influence of hydrogen sulphide, the colouring matters of litmus are decolorised, Kane's idea being, that a colourless hydrogen sulphide compound is thus formed. (V. also Malaguti, Ann. Chim. Phys. [iii.] 37, 206; Vogel, J. pr. Chem. [ii.] 16, 311.) Nascent hydrogen, and other reducing agents such as ferrous and stannous oxide, &c., decolorise them by reduction in the ordinary manner. Azolitmin thus yields colourless *leucazolitmin*, which, however, rapidly oxidises and becomes coloured on exposure to air. If stannous chloride is added to an ammoniacal solution of azolitmin, purple-coloured stannous-azolitmin is precipitated; if this is boiled with slightly acidulated water there is formed the colourless compound of stannic oxide with leucazolitmin, which, if exposed to air, changes into the bright scarlet stannic-azolitmin.

Deoxidising agents such as sulphurous acid and sulphites do not decolorise the colouring-matters of litmus.

Azolitmin and erythrolitmin, suspended in water and submitted to the action of chlorine gas, are decolorised and give yellow chlorine derivatives, *chlorazolitmin* and *chloroerythrolitmin*, substances insoluble in water, but soluble in alcohol, ether, and in alkalis.

In his earliest memoir, Kane (Annalen, 36, 324) mentions that on heating the colouring matters of litmus mixed with chalk or gypsum, a red vapour is given off which condenses in the form of crystalline scales (atmérythrin) soluble in alcohol. When heated alone, this substance is not produced. Although Kane makes no subsequent mention of this body it is possible that it was indirubin or even indigotin, since at a later date, Wartha (Ber. 9, 217) states that he found some samples of litmus to contain indigotin, recognisable by the violet vapour given off on heating a few cubes of the commercial product in a test tube. Its presence may have been due to the use of urine containing indoxyl in the preparation of the litmus.

Wartha (*l.c.*) gives the following results of his examination of litmus. The commercial product is well shaken up with alcohol; the filtered purple solution thus obtained has a green fluorescence, and exhibits in the spectroscope a characteristic absorption band in the green with an almost total absorption of the violet end. The colouring matter (*a*) itself is obtained on evaporating the solution.

The litmus residue insoluble in alcohol is digested for 24 hours with distilled water, and the filtered deep-coloured solution is evaporated to dryness. The extract thus obtained is repeatedly treated with absolute alcohol containing a little glacial acetic acid and again evaporated, so that all traces of water may be removed, and there finally remains a brown powdery mass. On extracting this with absolute alcohol, a large quantity of a scarlet substance (*b*) is dissolved. It is similar to orceïn and dissolves in ammonia with a reddish-purple colour. That portion of the brown powder which is insoluble in the acidified alcohol is dissolved in water, the filtered solution is evaporated to dryness, and the residue is repeatedly washed with absolute alcohol and evaporated in order to expel all traces of acetic acid. The residual brown powder, which is very soluble in water, with a reddish-brown colour, but insoluble in alcohol and in ether, is the purified and extremely sensitive colouring matter of litmus (*c*). Its alkaline solution is blue, its aluminium and tin lakes are violet, and its calcium and barium lakes blue. It appears to be very similar to Kane's azolitmin, but it is said not to contain nitrogen. The yield of these various colouring matters is as follows: (*a*) 2·3 p.c., (*b*) 3·4 p.c., (*c*) 5·7 p.c. (Mitchell, Chem. News, 1876, 140).

An examination of the colouring matters of litmus was also made by Rochleder and Skraup (Wien. Anz. 1874, 118; Chem. Zentr. 1874, 424). Other references are Magner, J. Pharm. Chem. 12, 118; Desfosses, *ibid.* 14, 487; Peretti, *ibid.* 14, 539.

Of interest also in connection with this subject is the fact that when ethyl-amino-orsellinic acid is oxidised by air in alkaline solution it yields an orange-coloured dye possessing basic properties (Heinrich and Dorschky, Ber. 1904, 37, 1416).

A peculiar blue colouring matter similar to litmus, and called *tournesol en drapeaux*, has long been manufactured at Grand-Gallargues, Département du Gard, France, from the *Croton tinctorium* belonging to the *Euphorbiaceæ*. Coarse linen cloth is steeped in the deep bluish-green sap expressed from the berries and the tops of the plant, then dried quickly in the open air, and exposed for 1–1½ hours between layers of straw to the ammoniacal vapours of lant or horse-dung (*aluminadon*), care being taken not to submit them to this influence too long. The cloth thus acquires a deep-blue colour. It is then steeped in the sap a second time and dried in air till it acquires a purple or dull green. These blue cloths are used by the Dutch farmers for making an infusion with which to impart a red colour to the outside of their cheese, the blue being changed to red by the lactic and butyric acids of the cheese.

According to Joly (Ann. Chim. Phys. [iii.] 6, 111) the colouring matter pervades the entire plant and is readily extracted therefrom by water heated to 50°–60°. On being evaporated, an azure-blue resinous mass remains. Acids change the blue colour of its aqueous solution red, and this blue is not restored by alkalis, the colour becoming thereby rather greenish. It is, therefore, probably quite distinct from the colouring matter of litmus. Possibly it is identical with the blue colouring matter which can be extracted from another plant belonging to the *Euphorbiaceæ*, viz. *Mercurialis perennis*. A. G. P.

LIVER-BLENDE *v.* ZINC-BLENDE.

LIVER OF SULPHUR. *Hepar sulphuri; potassa sulphurata.* This compound consists of a mixture of salts of potassium, chiefly the higher sulphide, and is prepared by fusing in a clay crucible a quantity of potassium carbonate with half its weight of flowers of sulphur. The fused mass is poured out on a greased flagstone and allowed to solidify, when it assumes a liver-brown colour; hence its name. It is alkaline, and acrid to the taste, and when quite dry is inodorous; but when moist it smells of sulphuretted hydrogen.

In medicine, it is given internally in cases of lepra and psoriasis; whilst externally it is used in the form of lotions, baths; as ointment in chronic skin-diseases, such as eczema, scabies, and pityriass. It is also largely used as a plant-spray.

LIXIVIATION. Lixiviation is the application of a liquid, generally water, to solid bodies for the purpose of extracting the soluble part. For instance, the preparation of pearl-ash by dissolving out the potassium carbonate from the wood ashes, and the preparation of sodium nitrate from the crude nitrate, of beet sugar by Schutzenbach's process, are all applications of water to extract the soluble part. The extraction of gold from the tailings obtained from the stamp batteries, by means of dilute potassium cyanide solution in the presence of air, affords another example of the process of lixiviation

In carrying out this process on a commercial scale, three things are sought to be attained: First, that the residue should be completely exhausted of soluble matter; second, that the solution obtained should be nearly saturated; and, thirdly, that the process should be continuous. A series of tanks is therefore provided, standing at the same level, and provided with false bottoms covered with a filtering bed, and with connecting tubes, pumps, and so on. Each of these tanks contains the substance to be lixiviated, and the water travels from tank to tank, increasing in saturation.

The process is so arranged that at any given moment a nearly saturated liquor is passing over a *fresh* supply of the substance, while clean water is running through the nearly exhausted residue. When the residue in any tank is completely exhausted it is removed, fresh stuff put in, and that tank made the last of the series. In some cases a pump is necessary between each tank to pump the liquid from beneath the false bottom into the next tank

If the solution formed is of high sp.gr., so much pumping is not necessary. One detailed description will suffice. In the preparation of soda by the Leblanc process, the black ash (roughly speaking, soluble sodium carbonate and insoluble calcium sulphide) is lixiviated. For this purpose, four or more iron tanks are used, built side by side, each about 10 feet × 10 feet × 6 feet. Each tank has a false bottom of perforated iron plates, and a large cock in the bottom, by which all the liquor it contains can be run off. It has also an overflow pipe, rising from below the false bottom and communicating with the next tank, and a second overflow pipe which communicates with a trough outside. The first tank is connected with the last by a pipe. Any of these pipes can be closed by plugs or cocks. Suppose the process to be in full working order. Fresh black ash, broken in large lumps, has been placed in tank 4, on a bed of cinders laid over the false bottom. Tanks 3 and 2 contain partially exhausted black ash, and tank 1 completely exhausted black ash (tank waste). The overflow pipe between 3 and 4 is opened, and a pump connected with 1, which pumps the liquor over into 2. It flows from 2 to 3, from 3 to 4, until 4 is full. Tank 1 is now cut off, emptied, cleaned, and a fresh supply of black ash put in. While this is going on, fresh water is flowing into 2, and sufficiently saturated liquor flowing away from 4 by the outside overflow pipe. 4 is now connected with 1. The liquor is pumped out of 2 into 3, flows from 3 to 4, from 4 to 1. When 2 is empty of liquor it is in the same way cleaned out, and a fresh charge put in, and so the lixiviation is kept continuous, strong soda solution running off at one end, and exhausted tank waste being removed at the other.

LOADSTONE. A name applied to those specimens of the mineral magnetite (*q.v.*) which are magnetic with polarity, and are thus capable of orientating themselves when freely suspended. All specimens of magnetite are readily attracted by a magnet, but only few exhibit polarity in their natural state. Such specimens are found in exposed situations in mountainous districts, *e.g.* in the Ural and Harz Mountains, where they have no doubt been magnetised by the electric discharges of lightning. Such stones were at an early period mounted in iron frames and used as natural magnets For historical details, *see* William Gilbert, De Magnete (1600; English edition with notes by S. P. Thompson, 1900). S P. Thompson on Petrus Peregrinus's Epistola de Magnete (Proc. British Acad. 1907, vol. ii.).

L. J. S.

LOBELACRIN *v.* LOBELIA.

LOBELIA, *Indian tobacco* (*Lobélie enflée*, Fr.; *Lobeliakraut*, Ger.). The official lobelia, *Lobelia inflata*, was described by Linnæus in 1741 (Acta Soc. Reg. Scient. Upsal. 1746) from specimens cultivated by himself, but he does not ascribe to it any medicinal properties. It is an annual herbaceous, somewhat pubescent plant, attaining a height of from 9 to 18 inches, with inconspicuous bluish racemose inflorescence. It is indigenous to the Eastern portions of N. America, and is cultivated in European gardens (Fluck. a Hanb. 399; Bentl. a. Trim. 162). According to J. U. and C. G. Lloyd (Pharm. J. [iii.] 17, 566), the first to employ lobelia in medicine was Thomson, an American herbalist of some notoriety about the end of the eighteenth century. The Indians, although they made use of the great lobelia, *L. syphilitica* (Linn.), were not acquainted with the *L. inflata*, as has been commonly supposed, and as one of its names would imply. The drug only gradually came into favour as an article of *materia medica*, and it forms the ethereal tincture of the British Pharmacopœia (1914). The herb should be gathered when, after flowering, some of the capsules have become inflated. In physiological action, lobelia resembles tobacco. It is an acrid narcotic poison, but in small doses is expectorant or emetic and is employed in spasmodic asthma and diseases of the respiratory organs. The seed is more active than the herb, but the latter is almost exclusively employed in medicine.

The plant was investigated by Colhoun in 1834 (J. Pharm. Chim. [ii.] 20, 545), but the first definite results were obtained by Proctor (Amer. J. Pharm. 9, 98; 13, 1). The seed was exhausted with spirit containing a little acetic acid, the solution evaporated, and the residue mixed with magnesia and extracted with ether. On evaporating the ether an acrid alkaloidal substance, *lobeline*, remained, which by conversion into acetate and treatment with animal charcoal, was obtained in a purer form. Lobelia was further studied by Pereira (Mal. Med. 2nd ed. 2, 584), Reinsch (Pharm. J. [i.] 3, 128), Bastick (*ibid.* [i.] 10, 217), F. F. Mayer (Amer. J. Pharm. 37, 209), Richardson (*ibid* [iv.] 2, 203), Lewis (Pharm. J. [iii.] 8, 561), Dragendorff and Rosen (Chem. Zentr. 1886, 873), J. U. and C. G Lloyd (Pharm. J [iii.] 17, 566, 686, 1037; 18, 135), Dresser (Arch. exp. Path u. Pharm. 26, 237), Wieland (Ber. 1921, 54, 1784).

Lobeline, according to J. U. and C. G. Lloyd, is a colourless, odourless, amorphous powder, extremely active, a very small quantity of its solution applied to the tongue causing immediate vomiting. Soluble in alcohol, chloroform, ether, benzene, carbon disulphide; slightly soluble in water. Oxidised by permanganate, it yields benzoic acid (Pachkis and Smits, Monatsh 11, 131). Salts of lobeline are soluble in water or alcohol, but, excepting the acetate, not in carbon disulphide. The aqueous solution is precipitated by alkalis and alkaloidal reagents. Its hydrochloride can be removed from its aqueous solution by repeated agitation with chloroform, and its final purification can be effected by crystallisation from alcohol, benzene, or ether Gives a crystalline platinochloride.

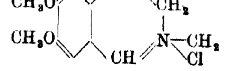
Lobeline, which, according to Dresser, is the only active constituent of lobelia, has the formula $C_{23}H_{29}O_2N$ (Wieland, *l.c.*). It crystallises in broad colourless needles, m.p. 130°–131°; $[\alpha]_D^{15} = -42{\cdot}85°$ in alcoholic solution. The sulphate, nitrate, bromide, and chloride are placed in order of increasing solubility in water; they are crystalline neutral salts. The base is monacidic. It is readily hydrolysed to acetophenone. Contains no ketonic or hydroxy groups; the lactone ring and methoxy group are absent. The nitrogen atom appears to be in the tertiary form.

Lobeline appears to occur in the plant in combination with *lobelic acid*. It is precipitated from an aqueous decoction of lobelia by copper sulphate, and may be separated by treatment with hydrogen sulphide and extraction with ether. Small acicular crystals, soluble in water, alcohol, or ether

Lobelidine $C_{20}H_{25}O_2N$ is isolated from the final ethereal mother liquors obtained during the preparation of lobeline, in the form of small irregular prisms, m.p. 106°. Its hydrochloride has m.p. 165° (decomp.).

LOBINOL. A poisonous, unsaturated phenol, having two hydroxyl groups in the ortho position, isolated by McNair (J. Amer. Chem. Soc. 1921, 43, 159) from the bark of *Rhus diversiloba*. An amber-red oily liquid giving acetyl and benzoyl and other derivatives.

LODAL. Trade name for 6-7-dimethoxy-2-methyl-3-4-dihydro*iso*quinolinium chloride



Used in medicine as a pressor substance.

LOESS (Ger. *Löss*). A pale buff-yellow, porous, friable, fine-grained material occurring in certain regions as extensive deposits, which are probably in most cases of æolian (wind-borne) origin. It consists of minute angular grains of quartz and other rock-forming minerals, flakes of mica without definite orientation (in rocks of aqueous origin the flakes of mica lie parallel to the bedding planes), and clayey and calcareous material in varying proportions. It therefore varies between wide limits in chemical composition as illustrated in the following analyses: I and II, Loess from the Mississippi valley; on material dried at 100°, the H_2O includes H from the organic matter (T. C. Chamberlin and R. D. Salisbury, 6th Ann Rep. U.S. Geol. Survey, 1884–85). III, Adobe from Santa Fé, New Mexico; also Cl 0·34. IV, Adobe from Salt Lake City, Utah; also Cl 0·11 (III and IV by L. G. Eakins, quoted by I. C. Russell, Geol. Mag. 1899). V, Loess from Bonn on the Rhine (G. Bischof, Chem. Geol. 1855; stated as $CaCO_3$ 17·63, $MgCO_3$ 3·02, MgO 0·21). VI, 'Black-earth' (chernozem) from Russia (R. Phillips in R. I. Murchison, Geology of Russia, 1845; also Cl 1·7, traces of humic acid, SO_3).

	I.	II.	III.	IV.	V.	VI.
SiO_2 .	72·68	60·69	66·69	19 24	62·43	69·8
TiO_2 .	0·72	0·52	—	—	—	—
Al_2O_3	12·03	7·95	14 16	3·26	7·51	13·5
Fe_2O_3	3·53	2·61	4 38	1·09	5·14	7·0
FeO .	0·96	0·67	—	—	—	—
MnO .	0·06	0·12	0·09	trace	—	—
CaO .	1·59	8·96	2·49	38·94	9·87	1·6
MgO .	1·11	4·56	1·28	2·75	1·65	—
K_2O .	2·13	1·08	1·21	trace	[1·75]	—
Na_2O .	1·68	1·17	0·67	trace		
P_2O_5 .	0·23	0·13	0 29	0·23	—	—
SO_3 .	0·51	0·12	0·41	0·53	—	—
CO_2 .	0·39	9·63	0·77	29·57	9·34	—
H_2O .	2 50	1·14	4·93	1·67	2·31	—
Org. mat.	0·09	0·19	2·00	2·96	—	6·4
	100·21	99·54	99·72	100·35	100·00	100·0

When rubbed between the fingers the material is soft and friable with a harsh feeling; but, owing to its homogeneity and lack of bedding, it can stand up as vertical cliffs some hundreds of feet in height. Loess is of wide distribution in the Rhine valley, and extends through central Europe and Asia into China; in the latter country reaching its maximum development and forming in places deposits of over 1000 feet in thickness. Throughout the Mississippi valley it is also a common surface deposit; and a very similar material, known as *adobe*, is widely distributed in the arid regions of the southwestern United States and Mexico. The material is much used for brick making, especially the sun-dried bricks of primitive peoples (hence the name adobe, which means in Spanish a sun-dried brick). The more calcareous varieties are used for mortars and cements. When containing much organic matter it forms a fertile soil, *e g.* the well-known *black-carth* or *chernozem* (tchernozem) of south Russia.

For further analyses, *see* H. G. Schering, Chemische Untersuchungen über Löss und Lehm, Diss. Freiburg.-i.-Br. 1909; P. Werling, Chemische Untersuchungen über den Löss der Pampas-Formation Argentiniens, Diss. Freiburg-i.-Br. 1911 L. J. S.

LOGWOOD. Logwood or Campeachy wood is one of the most important dyestuffs, and at the present time is very largely employed. Although for a long time it has successfully competed with the artificial colouring matters, its supremacy as a cotton dye has been affected to a considerable extent by the introduction of the sulphide blacks.

Logwood appears to have been first imported into Europe by the Spaniards shortly after the discovery of America, and has been cultivated in Jamaica from the year 1715 In the time of Elizabeth its employment as a dye was prohibited by Act of Parliament, and large quantities of the wood were burned, because it was said to produce fugitive colours.

It is derived from the *Hæmatoxylon campechianum* (Linn.), a tree which belongs to the family *Cæsalpiniaceæ*, and is a native of the warmer part of South America and some of the West India Islands. It also grows in the island of Mauritius, and trials indicate that this wood is of good quality (private communication)

Logwood usually comes into the market in large blocks weighing about 400 lbs. These externally are of a deep brown colour, but internally have a much lighter tint. The best qualities come from Jamaica, Honduras, and St. Domingo, for the true Campeachy wood, at one time esteemed to be the best, is now practically exhausted.

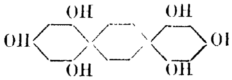
The colouring principle of logwood, *hæmatoxylin*, was first isolated in a crystalline condition by Chevreul (Ann. Chim. [ii.] 82, 53, 126), who obtained it by extracting the wood with ether, evaporating the extract, and digesting the residue with alcohol. After distilling off the alcohol the residue was allowed to stand in contact with water, when the hæmatoxylin separated in crystals. It may also be prepared by similarly treating commercial logwood extract which has been incorporated with a large quantity of sand (O. L. Erdmann, Annalen, 44, 292; J. pr. Chem. 26, 193; 36, 205; 75, 318). For this purpose ether containing water is preferable (Hesse, Annalen, 109, 332). It is, however, more easily obtained from the dark-coloured crusts which slowly separate when concentrated logwood liquor stands for some time in a cool place. The crude mass is ground to a fine powder, extracted repeatedly with ether, the ethereal solution evaporated, and the residue left in contact with water, when dark-coloured crystals separate, which by recrystallisation from water containing a small quantity of sodium bisulphite, may be obtained colourless (W. H. Perkin and Yates, Chem. Soc. Trans. 1902, 81, 236).

Pure hæmatoxylin crystallises in prisms with $3H_2O$, and is sparingly soluble in cold, readily so in hot, water. Its aqueous solution is coloured purple with alkalis, and this on exposure to air eventually assumes a brown tint. Hæmatoxylin is dextro-rotatory, a 1 p.c. aqueous solution having a rotation of 1·85 in a 200 mm. tube. It readily reduces salts of silver and gold, gives with alum a rose-red coloration, with iron alum a violet-black precipitate, and with neutral and basic lead acetate at first a colourless and then a blue deposit which darkens by air oxidation.

O. L. Erdmann (*l.c.*) was the first to submit hæmatoxylin to analysis, and proposed the formula $C_{40}H_{17}O_5$, which he subsequently altered to $C_{16}H_{14}O_6$. This latter formula was confirmed by Hesse (*l.c.*) and at the present day is accepted as correct.

By fusion with alkali, hæmatoxylin yields pyrogallol (Reim, Ber. 1871, 4, 331), and according to E. Erdmann and Schultz (Annalen, 216, 234) also formic acid. R. Meyer (Ber. 1879, 12, 1392) submitted hæmatoxylin to destructive distillation and considered that in this manner not only pyrogallol but also resorcinol is produced. According, however, to W. H. Perkin and Gilbody (Chem. Soc. Trans. 1902, 81, 245), no resorcinol is thus obtained.

Reim acetylated hæmatoxylin with acetyl chloride and prepared a substance which appeared to be the hexa-acetyl derivative $C_{16}H_8O_6(C_2H_3O)_6$, and as a result suggested the following constitution for this colouring principle:—



E. Erdmann and Schultz (Annalen, 1883, 216, 234) re-examined Reim's compound and showed that this was in reality a *penta-acetylhæmatoxylin* $C_{16}H_9O_6(C_2H_3O)_5$, m.p 165°-166°, and that hæmatoxylin therefore contains five hydroxyl groups. This result was confirmed by the work of Herzig (Monatsh. 1894, 15, 143), who, by the action of sodium methoxide and methyl iodide on hæmatoxylin, obtained the *tetramethyl derivative* $C_{16}H_{10}O_2(OMe)_4$, m.p. 139°-140°, a substance which still contains a hydroxyl group, since on treatment with acetic anhydride it yields *acetyltetramethylhæmatoxylin* $C_{16}H_9O_2(OMe)_4(C_2H_3O)$, m.p. 178°-180°. It was thus shown that hæmatoxylin like brazilin contains an alcoholic hydroxyl group which is not methylated by means of methyl iodide and sodium methoxide under the usual conditions, and indeed it has long been considered probable that these two colouring matters are closely allied in constitution (Liebermann, Ber. 1876, 9, 1883; *cf.* also Hummel and A. G. Perkin, Chem. Soc. Trans. 1882, 41, 373).

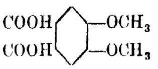
The following derivatives of hæmatoxylin have also been prepared: *Pentamethylhæmatoxylin* $C_{16}H_9O(OCH_3)_5$, plates, m.p. 144°-147° (Hertig); *dibromhæmatoxylin* $C_{16}H_{12}Br_2O_6$ (Dralle, Ber. 1884, 17, 373); *penta-acetylbromhæmatoxylin* $C_{16}H_8BrO_6(C_2H_3O)_5$, needles, m.p. 110° (Buchka, *ibid.* 1884, 17, 685); *penta-acetyltetrabromhæmatoxylin* $C_{16}H_5Br_4O_6(C_2H_3O)_5$ (Dralle); and *hæmatoxylinphthalein* $C_{40}H_{30}O_{14}$ (Letts, Ber. 1879, 12, 1652).

Our main knowledge of the chemistry of hæmatoxylin and the fact that it is in reality hydroxybrazilin is due to the elaborate researches of W. H. Perkin and his pupils, and their results have arisen mainly from a study of the oxidation products of hæmatoxylin tetramethyl ether.

According to this author (Chem. Soc. Trans. 1902, 81, 1059), tetramethylhæmatoxylin is most readily prepared by treating the solution of hæmatoxylin in alcoholic potash with methyl sulphate, a method which had previously been found serviceable by v. Kostanecki and Lampe

(Ber. 1902, 35, 1669) for the production of trimethylbrazilin from brazilin.

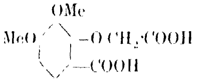
When tetramethylhæmatoxylin is oxidised with potassium permanganate (Perkin and Yates, *l.c.*), it yields *m-hemipinic acid*



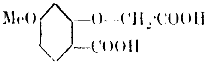
an important result, because it is thus certain that hæmatoxylin like brazilin (Gilbody, Perkin and Yates, Chem. Soc. Trans. 1901, 79, 1400) contains a catechol nucleus. Consequently, whereas in the molecule of brazilin a resorcinol and a catechol nucleus occur, in hæmatoxylin pyrogallol and catechol groups are present.

In addition to *m*-hemipinic acid, large quantities of a second acid $C_{11}H_{12}O_7$, m.p. 215°, are produced. This is *2-carboxy-5 : 6-dimethoxyphenoxyacetic acid* (1)—

(1)



(2)



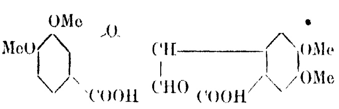
analogous to the *2-carboxy-5-methoxyphenoxyacetic acid* (2) which was obtained in a similar manner from brazilin trimethyl ether (*see* Brazilwood).

Finally, from the product of the oxidation a third compound *hæmatoxylinic acid* $C_{20}H_{20}O_{10}$, m.p. 180°, was isolated. This on reduction with sodium amalgam is converted quantitatively into an acid $C_{20}H_{20}O_9$, which is a monobasic lactonic acid, and it is therefore evident that the latter is produced in two stages thus :—

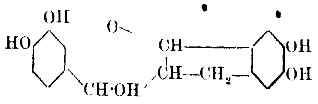
$$\underset{\text{Hæmatoxylinic acid}}{C_{20}H_{20}O_{10}}+2H=\underset{\text{Dihydrohæmatoxylinic acid.}}{C_{20}H_{22}O_{10}}$$

$$C_{20}H_{22}O_{10}-H_2O=\underset{\text{Lactone of dihydrohæmatoxylinic acid}}{C_{20}H_{20}O_9}$$

The constitution at first assigned to hæmatoxylinic acid by these authors was as follows :—

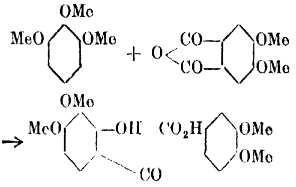


but this, and the corresponding hæmatoxylin formula—



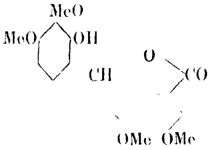
were subsequently modified, as the result of the synthesis of the lactone of dihydro-hæmatoxylinic acid referred to above (Perkin and Robinson, Chem. Soc. Trans. 1908, 93, 492).

When aluminium chloride reacts with a mixture of pyrogallol trimethyl ether and *m*-hemipinic anhydride, *2′-hydroxy-3′ : 4′ : 4 : 5-tetramethoxybenzoylbenzoic acid* is produced :—

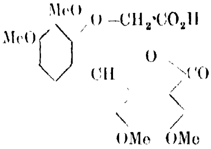


This ketonic acid is then converted by reduction with sodium amalgam into *2-m-meconyl-5 : 6-methoxyphenol* (1), which by treatment with chloracetic acid and sodium hydroxide gives the lactone of dihydrohæmatoxylinic acid (2).

(1)

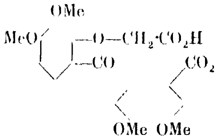


(2)

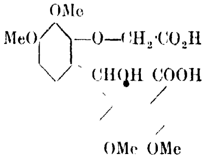


Consequently, the formulæ of hæmatoxylinic acid (3) and of dihydrohæmatoxylinic acid (4) are thus represented—

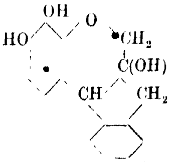
(3)



(4)



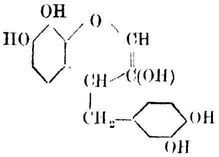
From these facts the constitution of hæmatoxylin itself naturally follows : —



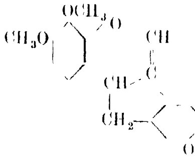
and this is identical with that which Pfeiffer (Chem. Zeit. 1904, 3, 380) from theoretical considerations suggested as possible.

Other constitutional formulæ have been

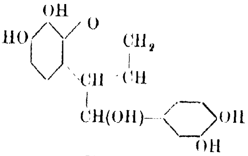
assigned to hæmatoxylin, of which that of Bollina, v. Kostanecki and Tambor (Ber. 1902, 35, 1678), analogous to the brazilin formula of Feuerstein and v. Kostanecki (Ber. 1899, 32, 1024), is of interest—



It was, however, evident that such an expression does not account for the production of *m*-hemipinic acid or 2-carboxy-5 : 6-dimethoxy phenoxyacetic acid by the oxidation of hæmatoxylin tetramethyl ether. On the other hand, v. Kostanecki and Lampe (Ber. 1902, 35, 1667) at first suggested that previous to the degradation of the methyl ether by oxidation with permanganate an internal linkage is produced, with production of the following compound :—



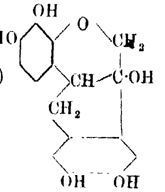
These authors ultimately considered, as W. H. Perkin contended, that a *m*-hemipinic residue is contained in hæmatoxylin tetramethyl ether, and as a result proposed the following modification of their formula for this colouring matter :—



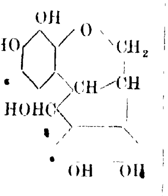
Hæmatoxylin.

Again, Herzig and Pollak (Monatsh. 1906, 27, 743 ; Ber. 1906, 39, 267), in a criticism of the earlier formula of Gilbody, Perkin and Yates (*l.c.*), suggested, among others, two possible constitutions for brazilin, the second of which is identical with that of v. Kostanecki and Lampe (*see* above), and which applied to hæmatoxylin, are thus represented :—

(1)



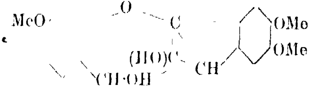
(2)



These formulæ of v. Kostanecki and Lampe and Herzig and Pollak cannot, however, be correct, as they do not account for the formation of hæmatoxylinic acid by the oxidation of tetramethylhæmatoxylin with permanganate (Gilbody, Perkin and Yates, *l.c.*).

Herzig (Monatsh. 16, 906) submitted acetyltetramethylhæmatoxylin to oxidation with chromic acid and obtained a new product, which on hydrolysis gave *tetramethyldehydrohæmatoxylin* $C_{16}H_5 \cdot O(OMe)_4OH$. This latter, on acetylation, yielded *acetyltetramethyldehydrohæmatoxylin* $C_{16}H_5O(OMe)_4(OC_2H_3O)$, and by methylation *pentamethyldehydrohæmatoxylin*.

W. H. Perkin (Chem. Soc. Trans. 1902, 81, 1057) oxidised tetramethylhæmatoxylin with chromic acid, and obtained a substance *tetramethylhæmatoxylone* $C_{16}H_6O(OMe)_4(OH)_2$, corresponding in all its reactions with trimethylbrazilone. For this, at that time, the formula

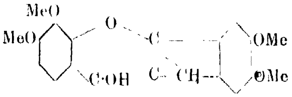


was proposed. In addition to this compound, 2-carboxy-5-6 dimethoxyphenoxyacetic acid and *m*-hemipinic acid were also produced during the oxidation. When digested with acetic anhydride, tetramethylhæmatoxylone gives *acetylanhydrotetramethylhæmatoxylone*

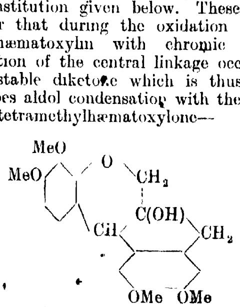
$$C_{16}H_5O(OMe)_4(OC_2H_3O)$$

evidently identical with Herzig's acetyltetramethyldehydrohæmatoxylin referred to above.

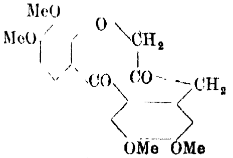
By hydrolysis this compound gave anhydrotetramethylhæmatoxylone $C_{16}H_5O(OMe)_4OH$—



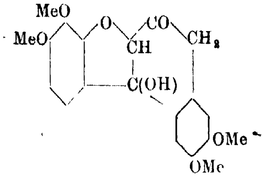
In a later paper Perkin and Robinson (Chem. Soc. Trans. 1908, 498) discarded these expressions and assigned to tetramethylhæmatoxylone the constitution given below. These authors consider that during the oxidation of tetramethylhæmatoxylin with chromic acid, a destruction of the central linkage occurs, and the unstable diketone which is thus formed undergoes aldol condensation with the production of tetramethylhæmatoxylone—



Tetramethylhæmatoxylin.



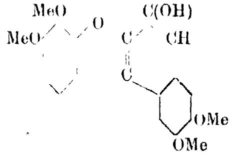
Diketone.



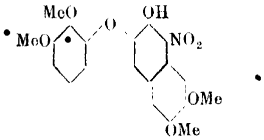
Tetramethylhæmatoxylone.

This formula indicates that tetramethylhæmatoxylone is a derivative both of coumaran and tetrahydronaphthalene.

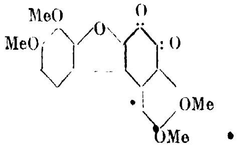
The formation of anhydrohæmatoxylone by means of acetic anhydride (*l.c.*) is due to the elimination of water from the aldol grouping in tetramethylhæmatoxylone, and the constitution thus given to this substance represents it as a derivative of β-naphthol, with which indeed it has many properties in common—



When acetylanhydrotetramethylhæmatoxylone is treated with nitric acid it readily reacts with the formation of the mononitro compound (Perkin and Robinson, *ibid.* 1909, 381)—



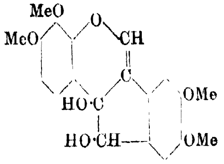
and from this substance by reduction with zinc-dust and hydrochloric acid the corresponding amino derivative is produced. This, when oxidised by ferric chloride, yields *tetramethoxy-α-brazanquinone* (*cf.* v. Kostanecki and Rost, *l.c.*)—



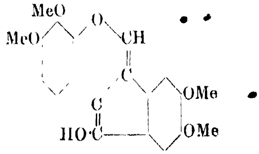
That this substance is an ortho-quinone is shown by its behaviour with *o*-tolylenediamine with which it condenses with formation of a characteristic quinoxaline. On reduction, the quinone is converted into the corresponding *dihydroxy* derivative.

v. Kostanecki and Rost (Ber. 1903, 36, 2202), on the other hand, proposed for the tetramethylhæmatoxylone (1) and anhydrotetramethylhæmatoxylone (2) of Perkin the following expressions which harmonised with their suggested constitution for hæmatoxylin (*l.c.*):—

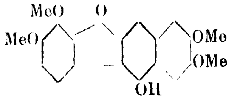
(1)



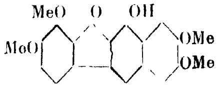
(2)



According to these authors, when tetramethylhæmatoxylone is treated with alcoholic sulphuric acid, a new compound (1′ or 4′) *hydroxy*-3 : 4 . 6′ : 7′-*tetramethoxybrazan* is formed, which is represented by one or other of the annexed formulæ :—

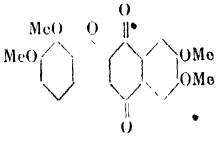


or

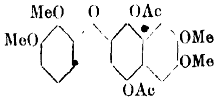


Oxidation with chromic acid converts this substance into 3 · 4 : 6′ : 7′-*tetramethoxybrazanquinone* (1), which by reduction and acetylation yields 3 : 4 : 6′ : 7′-tetramethoxy (1′ : 4′) diacetoxybrazan (2)—

(1)

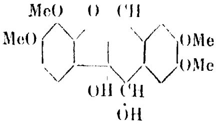


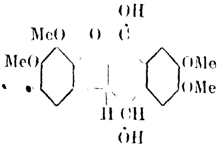
(2)



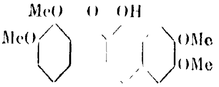
When distilled with zinc-dust, both hydroxytetramethoxybrazan and tetramethoxybrazanquinone yield *naphthalene.*

Herzig and Pollak (Ber. 1904, 37, 631) also found that cold concentrated sulphuric acid converts tetramethylhæmatoxylone into an isomeric compound *ψ-tetramethylhæmatoxylone,* and suggested the following formulæ as applicable to this substance :—

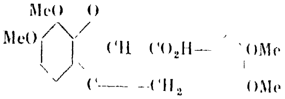




This by loss of water gives *β-anhydrotetramethylhæmatoxylone*, which is identical with v. Kostanecki and Rost's hydroxytetramethoxybrazan—

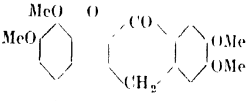


Perkin and Robinson (*l.c.*), as the result of a study of the work of Herzig and Pollak, have, however, shown that *ψ*-tetramethylhæmatoxylone is in reality a monobasic acid, and possesses the following constitution :—



This, by elimination of water, passes into the compound (1) and then by intramolecular change into hydroxytetramethoxybrazan (2) :—

(1)



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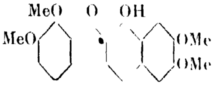
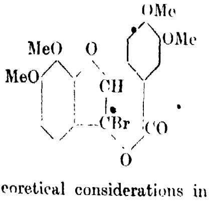


When *ψ*-tetramethylhæmatoxylone is treated with potassium hypobromite a colourless precipitate soon separates. This crystallises in almost colourless prisms or needles, and possesses the constitution of a *tetramethoxycumarono-iso-coumarinhydrobromide* :[1]—



For the theoretical considerations involved in the production of this interesting substance the original paper should be consulted.

Hæmatein.—When oxidised under suitable conditions, hæmatoxylin readily passes into the colouring matter hæmatein, according to the equation $C_{16}H_{14}O_6+O=C_{16}H_{12}O_6+H_2O$.

Hæmatein was first produced by O. L. Erdmann (*l.c.*) by passing air through an ammoniacal solution of hæmatoxylin, and subsequently acidifying with acetic acid.

Erdmann and Schultz (*l.c.*) who adopted a somewhat similar procedure, succeeded in isolating hæmatein in leaflets which possessed a metallic lustre. Reim, on the other hand (Ber. 1871, 4, 331), treated an ethereal solution of hæmatoxylin with a little concentrated nitric acid.

By extracting 'aged' logwood with ether, Halberstadt and Reis (Ber. 1881, 14, 611) obtained 1 p.c. of a very pure crystalline hæmatein.

Hummel and A. G. Perkin (Chem. Soc. Trans. 1882, 41, 373) exposed an ammoniacal solution of logwood extract to the air for two or three days. The precipitated ammonia compound of hæmatein was collected, dissolved in water, dilute acetic acid added, and the mixture digested on the water-bath to dissolve as much as possible of the suspended amorphous hæmatein. The clear liquid after partial evaporation deposited crystals of the colouring matter, possessing a yellowish green iridescence, and having the composition $C_{16}H_{12}O_6$.

According to Mayer (Chem. Zentr. 1904, 1, 228), hæmatein may also be prepared by oxidising hæmatoxylin in aqueous solution with sodium iodate.

Engels, W. H. Perkin and Robinson (Chem. Soc. Trans. 1908, 93, 1140) passed air for 6 hours through a solution of 15 grams of hæmatoxylin, dissolved in a solution of 16 c.c. of concentrated ammonia in 150 c.c. of water. The product of the oxidation was added in a thin stream to dilute acetic acid (250 c.c. of 10 p.c.) heated on the water-bath, when hæmatein separated in crystals.

Hæmatein is very sparingly soluble in water and the usual solvents. Alkalis dissolve it readily; ammonia dissolves it with a brown-violet colour, whilst its strong alkaline solution has a rich purplish-blue colour. On exposure to air the colour of these alkaline solutions gradually becomes red and finally brown, the colouring matter being destroyed. By addition of potassium acetate to the boiling alcoholic solution of hæmatein, the monopotassium salt $C_{16}H_{11}O_6K$ is deposited (A. G. Perkin, Chem. Soc. Trans. 1899, 75, 443).

Sulphurous acid or sodium bisulphite solution converts hæmatein into a colourless addition product, readily soluble in water, but no reduction hereby appears to occur, as on boiling the solution or by addition of acid hæmatein is precipitated. With zinc and hydrochloric acid or with stannous chloride and caustic soda, a solution of hæmatein is decolorised, but on standing the liquid regains its former tint.

It has long been considered that hæmatein is hydroxybrazilein, and this has now been clearly proved by a study of the behaviour of both hæmatein and brazilein with reagents under similar circumstances. This relationship is at once evident from a comparison of the following formulæ (Engels, Perkin, and Robinson):—

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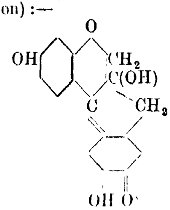
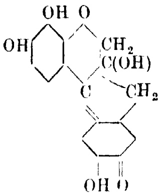
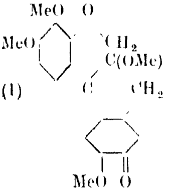
[1] ψ-trimethylbrazilone behaves analogously.


Brazilein.


Hæmatein.

When hæmatein is methylated by means of alkali and methyl sulphate, the product consists essentially of tetramethylhæmatein and pentamethyldihydrohæmateinol.

Tetramethylhæmatein (1) crystallises in amber prisms, and when digested with dilute potassium hydroxide is converted by the addition of water into *tetramethyldihydrohæmateinol* (2), yellow prisms—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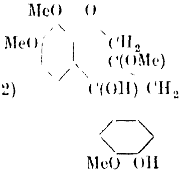
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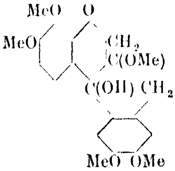
Pentamethyldihydrohæmateinol



the second product of the reaction, crystallises in yellow plates, and is also produced when tetramethyldihydrohæmateinol is methylated with methyl sulphate and alkali.

In the year 1882 Hummel and A. G. Perkin (Chem. Soc. Trans. 41, 367) observed that hæmatein and also brazilein are converted by the action of mineral acids into orange or red salts, from which the original colouring matters could not be regenerated.

When hæmatein is dissolved in cold sulphuric acid, a reddish-brown solution is produced from which, by cautious addition of acetic acid, minute orange-coloured prisms of *acid* iso*hæmateinsulphate* $C_{16}H_{12}O_5SO_4$ are deposited. The reaction may be represented thus:

$$C_{16}H_{12}O_6 + H_2SO_4 = C_{16}H_{12}O_5SO_4 + H_2O$$

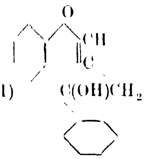
This substance, when left in contact with 80 p.c. alcohol, is gradually transformed, with loss of sulphuric acid, into a new compound crystallising in orange-red plates possessing a strong metallic lustre and to which the formula $(C_{16}H_{12}O_6)_2C_{16}H_{12}O_5SO_4$ was assigned. On the other hand, hydrochloric and hydrobromic acids in sealed tubes at 100° convert hæmatein respectively into iso*hæmatein chlorhydrin*

$$C_{16}H_{11}O_5 \cdot Cl$$

and iso*hæmatein bromhydrin* $C_{16}H_{11}O_5Br$, which crystallise in orange-red needles.

If to an aqueous solution of *iso*hæmatein chlorhydrin or bromhydrin silver hydroxide is added to remove the halogen, a solution of iso*hæmatein* is obtained, which on evaporation leaves this substance as an amorphous mass possessing a green metallic lustre. *Iso*hæmatein and its salts dissolve in solutions of the alkaline hydroxides with a red-violet colour which is easily distinguished from the corresponding blue-violet solution of hæmatein; moreover, the dyeing properties of these compounds and hæmatein differ considerably. Thus the *iso*hæmatein derivatives give, on cotton mordanted with alumina, a dull red inclining to chocolate, with strong iron a black, and with mixed alumina and iron a full chocolate. Again, the tinctorial power of these compounds is much greater than that of the original hæmatein, and the colours are much faster.

As the result of the investigation of a large number of pyranol salts (W. H. Perkin, Robinson, and Turner, Chem. Soc. Trans. 1908, 93, 1085), it seems certain that these hæmatein salts are derivatives of 4 : 3-*indenobenzopyranol* (1), and that *iso*hæmatein sulphate possesses the constitution (2)—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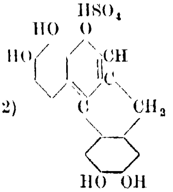
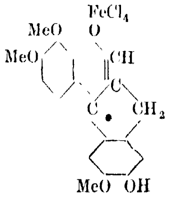
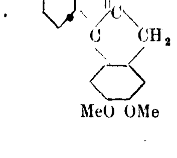

(2)

*Iso*hæmatein chlor- and bromhydrins are formulated similarly. Thus from tetramethylhæmatein, Engels, Perkin, and Robinson (*l.c.*) have prepared *5′-hydroxy*-7 : 8 : 4′-*trimethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *anhydroferrichloride*—



which crystallises from acetic acid in well-defined elongated prisms. Pentamethyldihydrohæmateinol, on the other hand, gives 7 : 8 : 4′ : 5′-*tetramethoxy*-4 : 3-*indenobenzopyranol* (1 : 4) *anhydroferrichloride*—



Before being used by the dyer, logwood is reduced to chips or powder, and these products are known as 'chipped,' 'rasped,' or 'ground' wood. When first cut down the wood has a pale yellow colour and contains only hæmatoxylin, but during transport or storage this colour gradually deepens owing to a surface oxidation of the hæmatoxylin into hæmatein. Formerly, and even to some extent at the present time, it was the practice to submit the chipped or rasped logwood to what is known as the 'ageing' process, in order to facilitate the hæmatein formation. This consists in wetting the wood thoroughly with water, then forming it into heaps, 4 to 5 feet high, in large airy chambers. Very soon the mass begins to ferment, which is indicated by a rise of its internal temperature, the wood gradually darkens in colour, and during the operation the mixture is repeatedly turned over and remixed in order to avoid too vigorous a fermentation and to obtain an even result. Constant attention is necessary during this 'ageing' process, for if the reaction is allowed to proceed too far, a portion of the colouring matter is destroyed, and 'burnt' or 'over-aged' wood is produced. In order to expedite this operation, the use of various oxidising agents has been suggested; a sprinkling of the wood with ammonia has been said to exercise a beneficial result; but, on the other hand, such processes are best avoided, for it is difficult under these circumstances to control the reaction and prevent an over-oxidation.

Latterly this ageing operation has been less in vogue, not only on account of the increased employment of logwood extract, but because it is now recognised that where the mordant employed for dyeing purposes can exert an oxidising action, this preliminary treatment is unnecessary. Formerly, logwood blacks on wool were produced by means of an iron mordant, but this is now largely replaced by the use of potassium dichromate, which provides a mordant possessing the power of converting at least a portion of the hæmatoxylin into hæmatein.

Logwood extract is now prepared in enormous quantity not only in this country but also in Jamaica in the neighbourhood of the logwood plantations, and in the latter case an economy is naturally effected in the carriage of some varieties of the extract rather than that of the more bulky wood to this and other countries. Logwood extract is almost invariably prepared from the 'unaged' wood, because whereas hæmatoxylin is readily soluble in water, hæmatein is not. On this account, an aged wood is difficult to exhaust. For the manufacture on the large scale, two processes are in vogue known respectively as the 'American' and 'French' methods. These differ merely in the manner in which the wood is lixiviated, for this is carried out by the French process in open pans with warm or boiling water, whereas in the American process, closed vessels are used in which steam at from 15 to 30 lbs. pressure is employed. In both cases the liquid is afterwards concentrated, preferably in vacuum pans, and the product is sold at about 15°Tw. as *logwood liquor*, at 51°Tw. as *logwood extract*, or in the solid condition as *solid logwood extract*. As a rule, it is considered that the extract made at the lower temperature gives the brighter shade.

Certain processes are in use for the 'ageing' of 'logwood liquor,' that is, the conversion of the dissolved hæmatoxylin into hæmatein. For this purpose the following methods have been suggested: (*a*) treat the logwood liquor with bleaching powder solution; (*b*) half neutralise with alkali or ammonia and blow air or oxygen through the liquid; (*c*) employ air or oxygen for this purpose without the addition of alkali; (*d*) boil with manganese dioxide (Weldon mud) and filter. Interesting also in this respect is the patented process of Haak (Chem. Zentr. 1905, ii. 867), who treats the extract with sodium nitrite.

A very important product more recently introduced is the so-called crystalline *hæmatein paste*, which is a treacly extract containing in suspension minute crystals of hæmatein. The details of the preparation of this material, which appears to have been first introduced from Jamaica, although now also manufactured in this country, are kept secret. For experimental purposes, this paste may be employed as the source of a comparatively pure hæmatein, which can be isolated from it by dilution with glacial acetic acid and subsequent filtration (private communication).

Logwood and its extracts are enormously employed for the dyeing of blacks on silk, wool, and to a less extent with cotton, chiefly in conjunction with iron and chromium mordants. It also enters into the composition of numerous compound shades.

Bastard Logwood.—During the past few years the growers of logwood in Jamaica have been greatly disturbed by the apparent increase on their properties of an unmerchantable variety of the tree known as 'bastard' logwood. Bastard logwood is practically devoid of hæmatoxylin, but contains instead a yellowish-green pigment which, when admixed with the commercial extract, reduces its characteristic tinctorial properties. Chips of the bastard logwood present a yellow, pale pink, white, or even chocolate coloured surface instead of the dark red or purple-bronze tinted colour of the best Jamaican or Mexican logwoods of commerce.

So similar are the trees of the 'true' and the 'bastard' logwood, that it is frequently impossible to decide whether a tree is really a 'mulatto' or not. When first cut a bastard tree is frequently dark enough internally to indicate that it is a good red-wood tree, but instead of darkening with age, as all the best wood does, it remains the same colour or becomes lighter rather than darker.

Chemical tests readily distinguish between the red and bastard wood, for whereas alkaline solutions turn an extract of true logwood a purple colour, with a bastard extract the shade of yellow is merely deepened. Again, mineral acids turn aqueous extracts of true logwood orange to bright red, whereas a bastard extract is not thereby affected.

Dyeing trials, employing stripe mordanted calico, are also serviceable, because, in the case of the bastard variety, the aluminium mordant remains practically colourless.

HÆMATOXYLON AFRICANUM.

The genus hæmatoxylon has hitherto been represented by only one species, the *H. campeachianum*, and the recent discovery of a South African species is of particular interest. This, now termed the *H. africanum*, was found among the rocks at Holoog in Great Namaqualand by Dr. H. H. W. Pearson in February, 1909, during the Percy Sladen Memorial Expedition in South-West Africa, 1909. It consists of a shrub 1–1·5 metres tall, the flowers of which are yellow, and the leaves smaller than those of the *H. campeachianum* (Stephens, Trans. Roy. Soc. S. Africa, 1913, [iii.] 2, 255).

Stems of this plant sent to England for examination were covered with a thin brownish bark, and varied from ½–1¼ inches in diameter, and from 11–16 inches in length. Cut transversely they were seen to consist mainly of a reddish-brown core surrounded by an almost colourless layer of wood, and this core, as is the case with logwood itself, darkened somewhat on exposure to air and became of a richer colour. When ground, the ochre-coloured powder is of a much lighter tint than either ground logwood or Brazil-wood.

The aqueous extract of the ground wood gives in comparison with those obtained from logwood and Brazil-wood the following colour tests:—

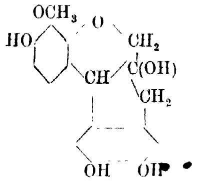
	H. africanum	Brazil-wood	Logwood
NaOH .	Pink	Crimson	Deep red-violet
$FeCl_3$.	Brown	Deep brown	Purplish-black
$Pb(Ac)_2$.	Pale pink almost colourless precipitate	Pink precipitate	Deep blue precipitate

The alkaline extract of the *H. africanum* on boiling deepens considerably in colour and possesses a faint greenish fluorescence, and this property is also exhibited by the corresponding extract of Brazil-wood.

Dyeing trials with both the *H. africanum* (170 p.c.) and Brazil-wood (40 p.c.) employing mordanted woollen cloth gave the following shades:—

	Cr	Al	Cu	Sn	Fe
H. africanum	Red-brown-violet	Dull bluish-red	Brown	Very pale brown	Dull purple
Brazil-wood	Red-violet	Bluish-red	Claret-brown	Red-brown very pale	Blue-violet

The *H. africanum*, therefore, differs from logwood in that the colouring principle it contains is not hæmatoxylin, but a substance which somewhat closely resembles brazilin in its general properties. It is a much poorer dyestuff than Brazil-wood, and on this account is of no technical importance, but should it eventually prove to contain brazilin, the matter is of special interest in view of the connection between this latter and hæmatoxylin which has been shown to exist by W. H. Perkin and his co-workers (*l.c.*). The slight difference in the properties of the *H. africanum* and Brazil-wood may be due to certain impurities in the former dyestuff not possessed by the latter, but on the other hand a methyl ether of hæmatoxylin of the type



will without doubt dye shades of an almost identical character with those given by brazilin itself (Perkin, J. Soc. Dyers. 1918, 34, 99).

LOKAO, a green dyestuff of Chinese origin, is, or rather was, since it has been supplanted by artificial colouring matters, met with in commerce in the form of thin laminæ of a dark bluish or bluish-green colour. Though formerly employed to some extent in Europe, it does not appear, owing to its extremely expensive nature, to have been extensively used. According to Crookes (Dyeing and Calico Printing, 429), lokao contains from 21·5 to 33 p.c. of ash, 9·3 p.c. of water, and 61·7 p.c. of colouring matter. It is insoluble in water, and the usual solvents, but dissolves in sulphuric acid with a red-brown coloration, and also in alkalis, but the solution thus obtained gradually acquires a brown tint.

According to Helot (Crookes, *l.c.*) and others, lokao requires for its preparation two distinct plants, the *Rhamnus dahurica* (Pall.) (hong. pi. lo. chou) and the *R. tinctoria* (Walldst. & Kit.) (pé. pi. lo. chou), the first of which is said to yield a deep and fast colour, whilst from the latter a weak but brilliant colour can be obtained. According to Rupe (Die Chemie der natürlichen Farbstoffe, 1900), the plant bark is extracted with hot water, the extract allowed to stand overnight, filtered, and then treated with potassium carbonate or milk of lime. Cotton yarn is immersed in this mixture, subsequently withdrawn and spread out in meadows overnight and a portion of the daytime, and the operation repeated ten or twenty times. The colouring matter is removed by rubbing the yarn with the hands in cold water, and the precipitate, which settles to the bottom of the receptacle, is washed by decantation, spread on paper and dried in the shade (*cp.* also Crookes, *l.c.*).

According to Cloez and Guignet (J. 1872, 1068) lokao or Chinese green is, in reality, a lake, and by treatment with ammonium carbonate is converted into the ammonium salt of the colouring matter *lokain* $NH_4{\cdot}C_{28}H_{33}O_{17}$. By the action of dilute sulphuric acid lokain is hydrolysed with formation of *lokaetin* $C_{18}H_{18}O_{10}$, glucose (rhamnose ?), and a soluble compound which is precipitated by basic lead acetate.

Kayser (Ber. 1885, 18, 3417; *cf* Rüdiger, Arch. Pharm. 1914, 252, 165) extracted finely powdered Chinese green with concentrated ammonium carbonate solution, added alcohol to the clear liquid, and thus obtained a precipitate of the crude ammonium salt of the colouring matter which he termed *lokaonic acid*. This was collected, extracted with ammonium carbonate, the solution precipitated by alcohol, and the operation repeated several times, the product being finally dissolved in water and the liquid evaporated to crystallisation with the addition of a little ammonia. Thus prepared the *diammonium* salt of lokaonic acid $C_{42}H_{44}O_{25}(NH_4)_2$ (Rüdiger) consists of small crystals possessing a bronzy lustre, which at 40° C. commences to lose ammonia, and at 100° gives the mono-ammonium salt $C_{42}H_{47}O_{27}(NH_4)$. The *potassium* salt

$$C_{42}H_{44}O_{27}K_2$$

separates in the form of a blue amorphous powder, when a concentrated aqueous solution of the diammonium salt is treated with alcoholic potash; whereas the *barium* salt $C_{42}H_{44}O_{25}Ba$, obtained by means of barium chloride, has a similar appearance, the lead salt $C_{42}H_{41}O_{25}Pb$ is a dark brown powder.

Lokaonic acid $C_{42}H_{46}O_{25}$, prepared by the decomposition of the diammonium salt with oxalic acid, consists of a bluish-black powder, which, when rubbed, develops a metallic lustre. It is insoluble in the usual solvents, but dissolves in solution of the alkaline hydroxides and ammonia with a pure blue tint. Treatment with sulphuretted hydrogen changes this to a blood-red colour, which passes to green on exposing the liquid to air. Digested with dilute sulphuric acid on the water-bath lokaonic acid is hydrolysed with formation of *lokanic acid* and a sugar rhamnose (Rudiger).

Lokanic acid $C_{36}H_{36}O_{21}$ is a violet-black crystalline powder insoluble in water, alcohol, ether, and chloroform, but soluble in alkaline solutions with a violet-blue coloration.

The *ammonium* salt $C_{36}H_{35}O_{21}NH_4$, the *barium* salt $C_{36}H_{34}O_{21}Ba$, and the *lead* salt $C_{36}H_{34}O_{21}Pb$, are described by Kayser.

Hot 50 p.c. potassium hydroxide solution converts lokanic acid into *phloroglucinol* and *delokanic acid* $C_{12}H_8O_5$, which consists of a brown powder dissolved by dilute alkalis, whereas nitric acid gives with lokanic acid *nitrophloroglucinol*.

The sugar to which Kayser gave the name of lokaose ($C_6H_{12}O_6$) is rhamnose $C_6H_{12}O_5$.

According to Persoz, cotton can be dyed in a weak alkaline solution of lokao, and it behaves also as a vat dyestuff, for which purpose it may be reduced by faintly acid or alkaline stannous chloride. The colour thus obtained is blue, and can be converted into green by the subsequent employment of a yellow dyestuff.

In order to dye cotton a green with lokao, Persoz recommends a bath prepared by adding the pigment to a solution of soap, whereas for silk Michel obtained excellent results by employing lokao and alum solution in the presence of lime salts. For Chinese and other methods of employing this dyestuff, *see* Crookes (*l.c.*), and Rupe (*l.c.*). A. G. P.

LÖLLINGITE or **LEUCOPYRITE.** Iron diarsenide $FeAs_2$ crystallised in the orthorhombic system, and isomorphous with marcasite (FeS_2) and mispickel (FeAsS). It contains on an average 67 p.c. of arsenic, with about 2 p.c. of sulphur; small amounts of cobalt (up to 6·4 p.c.), nickel, copper, silver, and gold are frequently present. With increasing sulphur it passes into mispickel, which it closely resembles in colour—silver-white to steel-grey with brilliant metallic lustre; but there is a wide difference in density—sp.gr. 7·1–7·4 (for mispickel 6·1). An extensive deposit of arsenical iron, consisting mainly of löllingite, occurs in serpentine at Reichenstein in Silesia, and has been worked since 1699. The annual production amounts to 15,000 tons, from which white arsenic, arsenic sulphide, and arsenic are produced, as well as 50–60 kg. of gold. Deposits in mineral veins are also worked for arsenic at Breitenbrunn in Saxony, Schladming in Styria, Lölling in Carinthia, and in the Anniviers valley in Switzerland. L. J. S.

LOMATIOL. This colouring matter, which is closely related to lapachol, has been obtained from the seeds of the *Lomatia ilicifolia* and *Lomatia longifolia*, which occur in Australia (N.S.W. and Victoria).

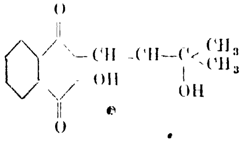
The colouring matter is obtained by extracting the seeds with boiling water acidified with acetic acid, and allowing the filtered extract to cool, when the product crystallises out. It is recrystallised from the same solvent.

Lomatiol $C_{15}H_{14}O_4$, yellow needles, m.p. 127°C., is easily soluble in alcohol or ether, in alkalis and alkali carbonates.

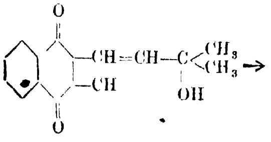
When heated with acetic anhydride and a trace of zinc chloride, it yields a *di-acetyl-derivative* $C_{15}H_{12}O_4(C_2H_3O)_2$, yellow needles, m.p. 82°.

The salts of lomatiol vary in colour from orange to brown, thus the silver salt, $C_{15}H_{13}O_4Ag,H_2O$ is brown, the calcium salt $(C_{15}H_{13}O_4)_2Ca$ is dark red, whilst the barium salt $(C_{15}H_{13}O_4)_2Ba,H_2O$ is orange.

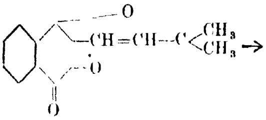
Rennie, who first examined this compound (Chem. Soc. Trans. 1895, 67, 784), was of the opinion that lomatiol was hydroxy-lapachol, but Hooker (Chem. Soc. Trans. 1896, 69, 1381), who continued Rennie's investigations, was able to show that it was *hydroxy-iso-lapachol*, and assigned to it the formula—

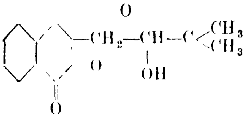


When lomatiol is dissolved in concentrated sulphuric acid, and left for some time, it passes into *hydroxy-β-lapachol* (3), red needles, m.p. 204°C., identical with that obtained from dihydroxy-hydro-lapachol by the action of the same reagent, whereas, if the reaction is stopped at an earlier stage, by pouring the solution of lomatiol in concentrated sulphuric acid into water almost as soon as solution is completed, an intermediate product, *dehydrolapachone*, is obtained to which Hooker gives the structure (2). The formation of these is shown thus:—



Lomatiol.

(2) 

(3) 

By careful oxidation of lomatiol, Rennie obtained acetic acid and phthalic acid.
A. G. P.

LONCHOCARPUS (*Lonchocarpus cyanescens*). The *Lonchocarpus cyanescens* (Benth.), a leguminous plant of the sub-order *Papilionaceæ*, is a woody climber from 10 to 14 feet long. The young leaves contain an indigo-yielding principle, and on this account the plant is employed by the tribes of Sierra Leone and the interior and those of Western Soudan as the source of a blue dye. In the former countries the young leaves are collected along with some more matured ones, roughly pounded and dried in the sun. In this state it is sent into the market as 'Gara,' and sold to the dyers. The natives of Western Soudan employ the young and tender buds, which are collected, pounded when quite raw, made into balls, and dried in the sun. For dyeing purposes the 'Gara' is covered with water, treated with potash and the bark of the *Morinda citrifolia* (Linn.), and left to ferment for some days. The cloth to be dyed is thrown into the vat, left there for some time, and dried in the sun. An examination of 'Gara' by Perkin indicated the presence of approximately 0·62 p.c. of indigotin (J. Soc. Chem. Ind. 1907, 389). Apparently also this plant is utilised in Northern Nigeria as a dyestuff in the form of a similar preparation to that described above, and for the manufacture of a crude indigo. A sample of this leaf product contained approximately 0·65 p.c. of indigotin, whereas in the indigo the presence of 21·47 p.c. of indigotin and 1·33 p.c. of indirubin was detected (Perkin, J. Soc. Chem. Ind. 1909, 353). The botanical examination of the former, and also of plant débris contained in the latter, by V. H. Blackman, indicated that they were derived from the *L. cyanescens*, or some closely related form. Rawson and Knecht (J. Soc. Dyers. 1888, 66) have described similar leaf and crude indigo products, which had been sent to this country by Sir T. Goldie, Governor of the Royal Niger Co., and these respectively contained 0·51 p.c. of indigotin, and 39·12 p.c. of indigotin, together with 4·75 p.c. of indirubin. A more recent examination of the leaf fragments in Rawson and Knecht's samples has shown that these possessed the same structure as those of the *L. cyanescens* (Perkin, *l.c.*), and it thus appears evident that in Western Africa this plant is extensively employed for dyeing and the preparation of indigo. There is reason to presume that the indigo-yielding principle present in the young leaves of the *L. cyanescens* gradually disappears when these reach maturity, as samples of the latter examined in this country were devoid of indigo-producing property. The *L. cyanescens* is probably identical with the 'Taroom akkar' described by Bancroft (Philosophy of Permanent Colours, 1813, i. 189 and 191).
A. G. P.

LONDON WHITE. *Flake white* (*v.* PIGMENTS).

LONGIFOLENE. A tricyclic sesquiterpene found by Simonsen in Indian turpentine obtained from the oleo-resin of *Pinus longifolia* (Roxb.). A colourless, somewhat viscous oil with a faint odour; b.p. 254°–256°/706 mm.; 150°–151°/36 mm; D^{30}_{30}; 0·9284; n^{30}_{D}; 1·495; M − 64·15 α_D + 42·73°. Does not yield a solid nitroso chloride, nitrosate, or nitrosite. Forms a hydrochloride as a crystalline solid, m.p. 59°–60°, $[\alpha]_D$ + 7·1 (chloroform). The hydrobromide has m.p. 69°–70°, and the hydriodide m.p. 71° (Simonsen, Chem. Soc. Trans. 1920, 578).

LOPHOPHORINE *v.* MEZCALINE.

LORANDITE. Sulpharsenite of thallium $Tl_2S \cdot As_2S_3$, crystallised in the monoclinic system, and one of the few minerals containing thallium (Tl 59·4 p.c.) as an essential constituent. The crystals are rich in faces, transparent, and of a deep cochineal-red colour with a metallic-adamantine lustre; streak, dark cherry-red. They are soft (H. 2–2½) and can be bent like gypsum. Sp.gr. 5·53; soluble in nitric acid with separation of sulphur. The mineral occurs with realgar at Allchar in Macedonia (southern Serbia), and has been detected with realgar and orpiment in the Rambler mine near Encampment in Wyoming.
L. J. S.

LORANSKITE. A rare-earth mineral containing Ta_2O_5 47, ZrO_2 20, Y_2O_3 10, Ce_2O_3 3, CaO 3·3, loss on ignition 8·15 p.c. It is black with a bright pitchy lustre and a greenish-grey streak. Sp.gr. 4·6, H. 5; optically isotropic. It is found as compact masses with other rare-earth minerals in pegmatite at Impilax in Finland.
L. J. S.

LORETIN. Trade name for *m*-iodohydroxyquinoline sulphonic acid ($C_9NH_4I(OH)HSO_3$) used as a germicide in surgical dressings (*v.* SYNTHETIC DRUGS and IODOFORM).

LOSOPHAN *v.* SYNTHETIC DRUGS and IODOFORM.

LOTUS ARABICUS. The *Lotus arabicus* (Linn.) is a leguminous plant, indigenous to Egypt and Northern Africa, and in the young condition is extremely poisonous. The subject has been investigated by Dunstan and Henry (Phil. Trans. 1901, 194, 515)

Lotusin, the active principle, can be isolated by extracting the dried plant with methyl alcohol. The extract is evaporated, the residue treated with water to remove chlorophyll and resin, and from the aqueous solution tannin and other impurities are precipitated by means of lead acetate. The filtrate, on evaporation, leaves a syrupy residue, from which crystals of lotusin slowly separate. In the pure condition lotusin $C_{28}H_{31}O_{16}N$ forms yellow needles, and when hydrolysed by digestion with hydrochloric acid, or by means of an enzyme *lotase*, also found in the plant, yields dextrose, lotoflavin, and hydrocyanic acid, according to the following equation:

$$C_{28}H_{31}O_{16}N + 2H_2O = 2C_6H_{12}O_6 + C_{15}H_{10}O_6 + HCN$$

When warmed with alcoholic potash (20 p.c.) lotusin is gradually decomposed with production of ammonia and *lotusinic acid* :

$$C_{28}H_{31}O_{16}N+2H_2O = \underset{\text{Lotusinic acid.}}{C_{28}H_{32}O_{18}}+NH_3$$

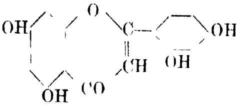
This compound is monobasic, gives yellow crystalline salts, and is hydrolysed by dilute hydrochloric acid with formation of *lotoflavin*, *dextrose* and *heptogluconic acid* :

$$C_{28}H_{32}O_{18}+2H_2O = C_{15}H_{10}O_6+C_6H_{12}O_6+C_7H_{14}O_8$$

Lotoflavin $C_{15}H_{10}O_6$ crystallises in yellow needles, soluble in alkaline solutions with a yellow colour. By fusion with alkali, *phloroglucinol* and *β-resorcylic acid* are produced.

With acetic anhydride lotoflavin gives a *tetraacetyl* compound $C_{15}H_6O_6(C_2H_3O)_4$, colourless needles, m.p. 176°–178°, and when methylated by means of methyl iodide the *trimethyl ether* $C_{15}H_7O_3(OCH_3)_3$ is obtained. This latter compound exists in two forms, viz. the α-form yellow rosettes, m.p. 125°, and the β-form glistening needles, m.p. 175°, which are mutually convertible. Both varieties give by means of acetic anhydride the same *monoacetyl lotoflavin trimethyl ether* $C_{15}H_6O_3(C_2H_3O)(OCH_3)_3$, yellow needles, m.p. 147°.

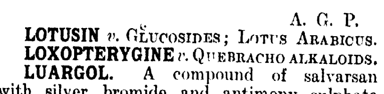
According to Dunstan and Henry, lotoflavin is probably a *tetrahydroxyflavone*, and possesses the formula :



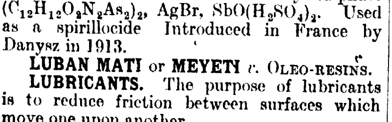
The hydrolysis of the cyanogenetic glucoside lotusin, with formation of maltose, lotoflavin and hydrocyanic acid, may also be expressed as follows :

$$C_{28}H_{31}NO_{16}+H_2O = C_{12}H_{22}O_{11}+C_{15}H_{10}O_6+HCN$$

The following constitutions are respectively assigned to lotusin (1) and lotusinic acid (2) :



I.



II.

A. G. P.

LOTUSIN *v.* GLUCOSIDES; LOTUS ARABICUS.

LOXOPTERYGINE *v.* QUEBRACHO ALKALOIDS.

LUARGOL. A compound of salvarsan with silver bromide and antimony sulphate $(C_{12}H_{12}O_2N_2As_2)_2$, AgBr, $SbO(H_2SO_4)_2$. Used as a spirillocide Introduced in France by Danysz in 1913.

LUBAN MATI or **MEYETI** *v.* OLEO-RESINS.

LUBRICANTS. The purpose of lubricants is to reduce friction between surfaces which move one upon another.

As the value of a lubricant depends almost entirely upon the conditions of speed and pressure under which it is used, and the nature of the surfaces with which it is in contact, it is necessary to outline the theory of lubrication before describing the preparation and properties of lubricating oils and greases.

Static friction. If two clean surfaces of the same metal, say lead, are pressed together they will adhere firmly. In cases where metals work together without lubrication this '*seizing*' is only prevented by the existence of a '*contamination film*' on the surface of the metal. Thus the so-called 'solid friction' observed in such cases is really the friction of surfaces lubricated by an extremely thin film (*e.g.* of air).

Thurston, experimenting with sperm and lard oils, found that the friction rapidly increased with pressure up to about 70 lbs., and then increased less rapidly or remained constant.

With plastic substances, *e.g.* axle grease, under ordinary loads the frictional coefficient is least when at rest and gradually increases with increasing speed owing to the resistance of the grease to shear.

With liquids the reduction of static friction depends on the thickness of the film which remains on the bearing surfaces under the loads commonly used. Different liquids vary much in this respect, and the effect seems to depend less on the viscosity of the oil than on its 'oiliness' (*v. infra*).

(*Cf.* W. B. Hardy and J. K. Hardy, Phil. Mag. 1919, 38, 32; Rayleigh, *idem* 1918.)

Low-speed friction. In this case the film of oil is so thin that the irregularities of the surfaces engage one another, causing abrasion. This does not matter if the surfaces are of proper materials, but in some cases it may lead to seizing of considerable areas and so much distortion of the surface that at higher speeds the formation of the 'pressure film' may be prevented and serious over-heating of the bearing may result.

The friction of lubricated bearings at low speeds is really solid friction, *i.e.* it is (1) independent of velocity and area of bearing surface, (2) proportional to pressure, and (3) dependent on the nature of the surfaces, which should be made of dissimilar metals.

Where a complete oil film cannot form, the oiliness of the lubricant is very important, but as the speed increases the oil film thickens and the friction depends more on the viscosity of the oil and less on its oiliness.

Friction, especially at moderate speeds, depends very much on the manner in which the lubricant is applied to the bearing. The best results are obtained with bath lubrication, and the friction increases as the free supply of oil to the journal decreases.

The coefficient of friction at very low speeds —0·0005–0·01 feet per minute—is often greater than the static coefficient, but the change from one to the other is continuous. From about 6·0 feet per minute the coefficient of friction steadily decreases with increase of speed.

High-speed lubrication. At a speed depending on the nature of the lubricant and on the load the surfaces begin to separate, and a comparatively thick 'pressure film' forms between them, being carried into the bearing on the surface of the moving part.

The maintenance of a pressure film between two plane and parallel surfaces depends upon the *inertia* and the *viscosity* of the oil, but in the case of plane surfaces inclined to one another—and this is the case met with in practice—the liquid wedges itself between them and forces them apart.

To this action is due the great carrying power of cylindrical bearings, which in use always wear so that the radius of curvature of the brass is greater than that of the journal. The two surfaces are thus inclined to each other, and the journal, as it rotates, carries the lubricant into the space between the journal and the brass, where it is wedged under a pressure which increases to a maximum at the point where the two approach most nearly.

In the design of bearings great care has to be taken that oil-ways are not cut in this neighbourhood of maximum pressure, or the pressure of oil which should carry the load is released and serious friction results.

The theory of the pressure film has been worked out in great detail, mathematically, by Osborne Reynolds, but only his general results can be given here. At speeds sufficiently high to ensure the formation of the pressure film the following laws appear to be very nearly true :—

(1) The friction is independent of the load ;

(2) The friction varies directly as the area of the contact surfaces ; directly as the speed ; and as the viscosity of the lubricant.

These are the laws of 'fluid friction.'

Above speeds of 100 feet per minute low speed effects are not observed and the friction is nearly proportional to the square root of the speed. This is probably due to lessened viscosity of the lubricant brought about by rise of temperature. From 190 to 790 feet per minute the friction is proportional to the fifth root of the speed, and above 1970 feet per minute it is practically independent of the speed.

With alternating pressures, especially when the alternations are rapid, *e.g* in the big ends of connecting rods, a given bearing will sustain much greater loads without seizing than it would if the pressure were continually in the same direction, because the oil is trapped between the surfaces at each reversal of the stress.

Friction in ball and roller bearings is practically independent of the presence of any lubricant, the chief function of the oil used being to prevent rusting of the polished surfaces.

A mineral oil of moderate specific gravity is therefore a suitable lubricant for such bearings.

COMMON LUBRICANTS.

Lubricants are divisible into four classes :

(*a*) Fats and liquid waxes ;

(*b*) Mineral oils ;

(*c*) Blended oils ;

(*d*) Greases and solid lubricants.

(*a*) **Fats and liquid waxes.** These are comprised under the name of fixed oils (*v.* OILS, FIXED, AND FATS). The fixed oils principally used as lubricants are : tallow oil, lard oil, neat's foot oil, olive oil, rape oil, and castor oil. For delicate machinery, such as clocks and watches, hazel-nut oil, ben oil, porpoise oil, and dolphin oil (blackfish oil) are used.

Sperm oil and Arctic sperm oil are liquid waxes, and are excellent lubricants because of their oiliness, and because their viscosity is less affected by temperature than is that of other oils.

The fixed oils are seldom used alone as lubricants except for textile machinery, in which there is a risk of the oil being splashed on the fabric. Mineral oils are very liable to make stains which cannot be washed out subsequently without injury to the material.

(*b*) **Mineral oils** are derived from crude petroleum, shale and lignite, and consist of saturated, unsaturated, and closed-chain hydrocarbons of b.p. over 300°. Those of sp.gr. up to 0·900 are usually distillation products, while those of sp.gr. higher than 0·910 are either 'reduced oils' or oils that have been distilled with steam *in vacuô*. Heavy oils that have been distilled under atmospheric pressure are unsuitable for use as lubricants because of the presence in them of products of 'cracking' (*v.* PETROLEUM AND SHALE OIL).

(*c*) **Blended oils.** Mineral oils are miscible with all fatty oils except castor oil, and mixtures containing 20-30 p.c of good fixed oil, *e.g.* sperm oil, are the best lubricants available for ordinary loads and speeds. Blown oils (partially oxidised oils) are soluble in mineral oils, and are sometimes used to give body to the lighter grades, but such blended oils have a great tendency to gum, and, though cheap, are not to be recommended.

(*d*) **Greases and solid lubricants.** The chief solid lubricants are graphite, soapstone (talc, steatite, French chalk), mica, and asbestos. These are seldom used alone, but are usually incorporated in a grease, the advantage being that under ordinary conditions the frictional resistance is merely that due to the resistance to shear of the grease, while under excessive pressure, though the grease may melt and run off the bearing, the solid lubricant remains and prevents damage. Filling materials, such as barytes and chalk, are sometimes added to greases, but they are not lubricants, and their addition is detrimental.

Anti-friction metals (*v.* ANTIMONY) may be regarded as solid lubricants, but their chief purpose is to afford a material into which the shaft can bed itself quickly

Greases may be natural fats, *e.g.* tallow, but are more commonly prepared by adding to mineral or fixed oils alkali metal soaps or, more often, aluminium, lime or lead soaps of fatty acids or resin acids. Such greases frequently contain a considerable quantity of water, but if this is thoroughly incorporated in the grease it has no bad effect upon its properties as a lubricant.

Boiled greases are prepared by dissolving lime soap in mineral oil ; they are very good for medium and heavy machinery.

'**Set**' or **axle greases** are made by adding to a mixture of mineral oil (100 gallons) and good slaked lime (500 lbs.), called the *lime part*, a certain proportion of resin oil (2–25 p.c.), called the *set*. The mixture is run at once into the packages in which it is to be sold, and in a short time sets to a solid or semi-solid mass, according to the proportion of resin oil added (*v.* also Archbutt, J. Soc. Chem. Ind. 1901, 1193).

Cup greases are prepared by saponifying fat, usually horse-fat, with freshly slaked lime in a large kettle heated by a steam jacket and provided with a mechanical stirrer. The usual proportions are 2000 lbs. fat, 200 lbs. lime, and 140 gallons of water. When saponification is complete and the excess of water has evaporated, a light-coloured mineral oil, sp.gr. 0·885–0·910 (about 100 gallons), is sprayed on the contents of the kettle until the right consistency is attained. The oil must previously be heated to 190°F.

Engine greases are made by incorporating cold mineral oil with hot soluble soda or potash soap. It is important that the soap should be neutral (Redwood)

Thickened mineral oils are often made by incorporating aluminium oleate with a light oil. The soap is made as follows: 112 lbs. oleic acid is mixed with 20 gallons hot water and a solution of 16¼ lbs. 77 p.c. caustic soda in 10 gallons water, and boiled until the formation of sodium oleate is complete 70 lbs. alum, dissolved in 20 gallons water, are then added to the solution, when aluminium oleate separates in greasy masses. It is freed from moisture by pressure (Hurst)

Railway waggon grease is usually composed of tallow, palm oil, soap, and water; and is prepared by heating the tallow and palm oil to 180°F., and running in a solution of sodium carbonate at 200°F. The whole is stirred well and run into tubs to set. It is usual to vary the composition of the grease according to the season of the year; the following are typical formulæ:

	Summer	Medium	Winter
Tallow . .	22	20	18
Palm oil . .	12	12	12
Sperm oil . .	1	1·5	2
Soda crystals .	5	5	5
Water . .	60	61·5	63
	100	100	100

The grease in use on the Midland Railway is prepared by dissolving 6 cwt of palm oil in 12 cwt. of water and adding to the solution 6 cwt. of tallow and 2 cwt. of dark mineral oil.

Another English railway grease: —

	Summer	Winter
Tallow . .	504 parts	420 parts
Palm oil . .	280 ,,	280 ,,
Sperm oil .	22 ,,	35 ,,
Caustic soda .	120 ,,	126 ,,
Water . .	1370 ,,	1521 ,,

Other preparations are made of tallow with colza oil, soda, and water in various proportions; and, for fine machines, of tallow with castor oil, &c., &c.

Palm-oil lubricants. Although palm oil may be used alone, its melting-point is too low for most purposes; to correct this, tallow and other fats are added to the amount of one-third or one-half of the total weight of the lubricant. A small quantity of soda should form a part of these lubricants, as by its use the free fatty acids which are contained in palm-oil are saponified and their action on the metals with which they come in contact is destroyed. Soda also is the medium by which water is introduced into the mixture.

Lead-soap lubricants. Lead salts yield on saponification with fats solid combinations called lead-soaps; they are hard at low temperatures, viscous at ordinary temperatures, but sufficiently fluid on heating by friction The melting-point of lubricants prepared from these substances is high, and they are therefore less suited for high speeds. So-called 'anti-friction lubricants' are composed of lead-soaps A basic lead acetate (sugar of lead) is combined with the requisite quantity of fat in the following manner. The lead solution is thus prepared: Sugar of lead 10 parts, litharge 10 parts, and soft water 110 parts, are boiled with frequent stirring for an hour and a half or two hours. The mass is then allowed to rest, and the clear fluid drawn off and restored to 100 parts by the addition of water. It is then heated to from 145°F. to 165°F. and immediately mixed with ordinary fat (colza oil, lard, and sometimes neats-foot oil), as, e.g., solution of sugar of lead 100 parts, colza oil 80 parts, lard 80 parts The preparation should show a uniform grey colour, and, after melting, congeal at from 100°F. to 122°F. (Brannt).

Soap lubricants. Ordinary soft soap, or fat combined with potash, is serviceable for some purposes, but is liable to have a part of the potash lye not fixed, by which damage is done to metals.

The following are from Brannt (Practical Treatise on Animal and Vegetable Fats and Oils).—

Caoutchouc lubricants for belts. Caoutchouc 20 parts, linseed oil 1000 parts. Melt the caoutchouc together with the same quantity of linseed oil, and as soon as the mixture commences to evolve vapours, stir in 20 parts of linseed oil and afterwards add the remainder of the oil by instalments of 100 parts.

Asphaltum waggon grease. Asphaltum 32 parts, black pitch 8 parts, petroleum 8 parts, litharge 8 parts, water 80 parts.

Naphthalene grease. Naphthalene 100 parts, colza oil 50–100 parts. Crude naphthalene is used.

Resin lubricant. Common resin 100 parts, resin oil 50 parts, lard 300 parts.

Graphite waggon grease. Tallow 36 parts. lard 9 parts, palm oil 9 parts, graphite 2 parts.

Graphite lubricants for quick-moving axles. Tallow 100 parts, graphite 100 parts; especially adapted for shafts revolving with great velocity without great load, as circular saws, ventilators, &c.

For this purpose natural graphite which frequently contains a large proportion of mineral matter is not so well suited as that produced by the Acheson process by heating anthracite at about 4000°C. This is reduced by machinery to a powder of such fineness that when suspended in liquids it exhibits the Brownian movement and cannot be separated by filtration, and when mixed with oil forms an emulsion, and does not subside on standing. It comes into commerce made into a paste with water (aquadag); fat (gredag); and oil (oildag). The first serves for the preparation of aqueous emulsions for cooling and lubricating boring and turning machinery, the second is used for cog-wheels and stuffing-boxes, and the third, when well mixed, to the extent of ½ p.c., with acid-free machine or cylinder oil, can be used for the running parts of machinery.

Lubricant for cutting tools. This is usually a solution of soft soap and soda in water.

PHYSICAL PROPERTIES AND TESTING OF LUBRICANTS.

A. **Viscosity.** For methods of determining viscosity, *see* PETROLEUM. The methods there given are equally applicable to all lubricating oils.

The determination of the consistency of fats and greases is of importance, but the methods available are entirely empirical.

In *Kissling's apparatus* a pointed rod of glass or metal, weighted at the top, slides vertically through a hole in a fixed plate. The point of the rod presses on the surface of the grease contained in a small beaker, and the time taken for it to penetrate a definite distance into the fat is a measure of the stiffness of the latter.

Kunkler's apparatus consists of a metal cylinder having an orifice at the lower end through which the grease is squeezed by a weighted piston. The whole apparatus is surrounded by a water-jacket so that the temperature of the test can be regulated.

In any determination of the consistency of fats, great attention must be paid to the preliminary treatment they receive, as they are extremely sensitive to mechanical disturbance and to change of temperature. After the grease has been placed in position it is necessary to leave it for 24 hours before proceeding with the test

B. **Specific gravity.** This property is used as an indication of the nature and purity of oils, and it forms the basis of the classification of the mineral oils. There is, however, no necessary connection between sp.gr and lubricating power; *e.g.* it is well known that mineral oils commonly have less lubricating power than fatty oils of the same sp.gr. (*see* also PETROLEUM AND SHALE OIL).

The sp.gr. of oils may be determined by the sp.gr. bottle, by the Sprengel tube, or by the Westphal balance, but with viscous oils these methods are liable to be tedious, and hydrometers are commonly used for the purpose.

It is frequently necessary to know the density of an oil at a temperature at which it cannot conveniently be determined experimentally; it can then be calculated with sufficient accuracy (1 in 4000) from the following formula, if the density of the oil at 60°F. is known: $D=d-kt$, where d=the density of the oil at 60°F.

$$k=\begin{cases}0{\cdot}000368 \text{ for a fixed oil,}\\ 0{\cdot}000367 \text{ for a Scotch mineral oil,}\\ 0{\cdot}000345 \text{ for a Russian mineral oil,}\\ 0{\cdot}000350 \text{ for an American mineral oil,}\end{cases}$$

t=the number of degrees above 60°F., and D=the required density.

C. **Flash-point.** This is the temperature at which the oil gives off sufficient vapour to form an explosive mixture with air in the standard apparatus employed (for details *see* PETROLEUM). It is usually stated that only oils of flash-point over 350°-400°F. should be used as lubricants, but the loss on evaporation is at least as good a test.

D. **Volatility.** It is obviously desirable that lubricating oils should not evaporate to any considerable extent at the temperatures at which they are used. The fatty oils are satisfactory in this respect, but mineral oils frequently contain as much as 15 p.c. of hydrocarbons volatile at 100°C.

Archbutt's apparatus for the determination of this loss consists of a copper tube placed horizontally across an air-bath by which it can be kept at any desired temperature. The oil to be tested, usually 0·5 gram, is placed in a platinum tray within this tube and subjected to a current of air, previously heated to the temperature of the bath, passing at the rate of 2 litres per minute for exactly 1 hour.

In some cases the oil is tested in a current of steam, but the procedure is quite similar to that when air is used.

As an example of its use, an oil intended for cylinders working at 160 lbs. pressure is tested at 370°F. when it should not lose more than 0·5-1·0 p.c. of its weight. With machine oils and spindle oils, even at much lower temperatures, the permissible loss is much greater.

E. **Setting-point** (the *cold test*). With most oils this is taken as the temperature at which they cease to flow, but in the case of Scotch shale oils the setting-point is the temperature at which solid paraffin is first deposited.

The oil, contained in a corked tube, is cooled in water, or in ice and salt, until it ceases to flow on reversing the tube. It is necessary to maintain the temperature constant for about 20 minutes before observing the condition of the oil (*v.* Salkowsky, J. Soc. Chem. Ind. 1888, 37; and Holde, *ibid.* 1890, 112; 1896, 138, 160), and in Hofmeister's method this is attained by using solutions of various salts, of such concentrations that they are saturated at their freezing-points. The result is that freezing takes place with formation of a eutectic mixture, and the temperature remains constant till the whole is solidified.

Schultze's method, used in Germany, depends on finding the temperature at which the oil flows through a tube of 6 mm. diameter at a rate of 10 mm. per minute under a pressure equal to 50 mm. of water.

F. **Melting-point of fats** and **greases.** This is frequently of importance, as a grease loses its power of reducing friction under great pressure should it become liquefied. As in the case of determination of consistency, attention must be paid to the preliminary treatment of the grease, and it should, in most cases, be left undisturbed for 24 hours before the test is made.

Many methods are used, most of which depend on observing the temperature at which the grease begins to flow under its own weight (*v.* Bensemann, J. Soc. Chem. Ind. 1885, 535; Cook, Chem. Soc. Proc. 1897, 74).

G. **The colour of oils** is of some importance, and Redwood uses Lovibond's tintometer (*v.* art. COLORIMETERS) for making a numerical record of this characteristic. Most mineral oils exhibit a fluorescence, usually of a blue or green colour, but this is not of much importance as a test (*v.* PETROLEUM).

H. **Oiliness.** The most important property of oils and greases which are to be used under conditions of low speed and high pressure (under 100 feet per minute and over 70 lbs. per square inch), is that called '*oiliness*' (*unctuosity, lubricity*). It depends on (1) interfacial action, which causes oils to spread themselves over metallic surfaces, and (2) on the power of the film to resist disruption.

It seems to be connected with the presence of unsaturated compounds which constitute 20–40 p.c. of most lubricating oils. It would appear that the unsaturated molecules of the lubricant enter into a firm physico-chemical union with the metallic surfaces, forming a friction surface which is a compound of oil and metal. Those oils which have the smallest coefficient of friction are found to be the best lubricants in practice (Deeley, Proc. Phys. Soc 28, 11, 1919).

Oiliness may be defined as the power of a lubricant to maintain an unbroken film under a heavy load: it cannot be measured in any exact way, and information as to the extent to which any given oil possess this property may best be obtained by properly conducted tests on mechanisms resembling those on which it will be used. Oiliness would seem to depend upon the effect of the lubricant upon the surfaces with which it is in contact rather than on any particular physical property of the lubricant This property is not necessarily connected with viscosity, being possessed in much greater degree by fixed oils than by mineral oils of the same viscosity. Moreover, different mineral lubricating oils of the same viscosity give very different frictional results. This is the reason that mineral oils must be blended with fatty oils to get the best lubricants for ordinary machinery. The amount of the admixed fatty oil need not be large. Stanton and Hyde found that a small proportion of rape oil had almost as marked effect upon the friction as a much larger percentage.

Oil-testing machines are made of many different designs, and may be used to investigate:

(1) Comparative oiliness or greasiness of lubricants;

(2) Frictional effects due to viscosity;

(3) Effects of temperature on friction;

(4) Effects of different loads;

(5) Effects due to varying speeds;

(6) Effects produced by different metals working in contact;

(7) Effects resulting from different methods of applying the lubricant.

Most of those effects, except (1), are amenable to calculation, or can be more easily determined in some other way; Nos. (6) and (7) are rather concerned with the design of bearings than with lubricants.

In most machines an experimental journal runs in brasses loaded in a manner which can be regulated by the operator, *e.g.* by a spring. The detailed description of such machines hardly falls within the scope of this article, and it is sufficient to say that Thurston's oil-testing machine is largely used (for a detailed description, *see* Archbutt and Deeley, Lubricants and Lubrication, 332; Hurst, Lubricating Oils, Fats, and Greases, 254 *et seq.*). Machines of similar type are those of R. H. Smith, A. Martins, Ingham and Stapfer, Stroudley, Goodman, and Lahmeyer (A. and D. chap. ix.).

These testing machines all suffer from the disadvantage that, at the speeds at which they are usually run, the frictional effects observed are due solely to the viscosity of the oil used, and therefore only give information as to that property; information which could better be obtained with a viscosimeter.

Machines of what is known as the *disc and collar* type are of much more use in investigating the 'oiliness' of lubricants. In them the oil is fed between a rotating disc and a stationary plate, a load is applied to force the two together, and low speeds are used. The best known machines of this class are MacNaught's, Woodbury's, Deprez and Napoli's, and Tower's.

Bailey's pendulum oil-tester is specially designed for use with oils intended for watches, clocks, and other small machines.

CHEMICAL PROPERTIES OF LUBRICANTS.

The chemical methods used for the examination of lubricants are those used for oils in general (*v.* PETROLEUM; AND OILS, FIXED, AND FATS).

The chemical properties of oils which are of special importance with reference to their use as lubricants are: (1) corrosive action on metals, which is closely connected with the acidity of the oil; (2) their tendency to gum or resinify; and (3) their liability to decomposition under the conditions of use.

(1) Most fatty oils, even when freshly prepared, contain some fatty acid, the amount of which increases with time of storage of the unrefined oil. This cannot be avoided, and is one of the chief reasons that such oils have been largely superseded by mineral or blended oils. The addition of resin or resin oil to a lubricant will often increase the acidity owing to the resin acids present.

In the case of mineral oils consisting essentially of hydrocarbons it has been surmised that their lubricating value depends upon the presence of unsaturated molecules (Dunstan and Thole). Apparently the same is true in regard to fatty lubricants. It has been shown that free fatty acids, in limited amount, greatly improve the friction reducing values of mineral oils and that the improvement in 'oiliness' or lubricating power of a mineral oil, by mixing with it a fixed oil, is mainly due to the small quantity of free fatty acid than to the neutral glyceride (Wells and Southcombe, J. Soc. Chem. Ind. 39 (1920), 53 R; Archbutt, *l* c.).

Crude petroleum normally contains small amounts of organic acids, but refined mineral oils ought to be practically free from acidity. In many cases where they do not conform to this standard they are found to contain free sulphuric acid, which has been left in the oil owing to imperfect washing after refining with acid.

The extent of the corrosive action of an oil on metals is proportional to its acidity, but is conditioned by the access of air or water to the metal. In absence of air and water even a grease containing 70 p.c. of fatty acids has little or no action on metals (Burstyn, Dingl. poly. J. 217, 314; Redwood, J. Soc. Chem. Ind. 1886, 362; Fox, Analyst, 1883, 8, 116; Donath, J. Soc. Chem. Ind. 1895, 283). The acidity is usually determined by titration, and is expressed in terms of alkali required to neutralise it, or as oleic acid.

(2) The *tendency to gum* in the case of fatty oils is closely associated with their drying properties Such oils as linseed oil are impossible as lubricants. The semi-drying oils are not used as lubricants with the single exception of rape oil, the least oxidisable, which is largely used owing to its low cost.

A rough idea of the drying properties of oils can be obtained by coating them on pieces of clean glass and observing the length of time they take to set, or to arrive at the same consistency. Another way is to place drops of the oils at the upper end of an inclined steel plate, and observe the distances they travel before coming to rest. Care must be taken to distinguish those cases in which the thickening of an oil is due to its acidity, the corrosive action resulting in the formation of metallic soaps which dissolve in the oil.

Mineral lubricating oils can absorb small quantities of oxygen at a high temperature (Bach, J. Soc. Chem. Ind. 1889, 990; Ostrejko, J. Soc. Chem. Ind. 1896, 26, 345, and 645), but under ordinary conditions such oxidation is practically *nil*. Any tendency to gum in this case is due to evaporation of the lighter constituents with deposition of asphaltic and tarry matters (Holde, J. Soc. Chem. Ind. 1894, 668; 1895, 894). The amount of bituminous matter present can be determined by extraction with light petroleum (Bender, J. Soc. Chem. Ind. 1891, 354). Closely associated with the gumming tendencies of oils is their liability to cause spontaneous combustion of cotton waste, &c., with which they come in contact. For this reason mineral oils have entirely superseded fixed oils in many cotton mills.

(3) The danger of *decomposition* is present in those bearings which run at a high temperature, *e.g.* hot neck rolls, but the commonest case where this has to be considered is that of cylinders of steam, gas, and oil engines. For these pure fixed oils should never be used, as in presence of steam they are hydrolysed to glycerol and fatty acids which rapidly corrode the cylinder and piston, forming large lumps of metallic soap. Steam cylinders are best lubricated with 'reduced' mineral oils of high viscosity, density, and flash-point, but very satisfactory results are obtained in practice by using lighter grades of mineral oils containing up to 30 p.c. of fixed oils or 'blown oils.'

For the lubrication of the cylinders of gas and oil engines a pure mineral oil should be used, preferably one which will evaporate without leaving any residue. The high temperature of the walls of such cylinders and the presence of flame cause such carbonisation of the oil and, unless care is used in its selection, this may cause serious trouble.

See OILS, FIXED, AND FATS; PETROLEUM; also Encyclop. Britt. 1910, arts. Lubricants and Lubrication; Archbutt and Deeley, Lubrication and Lubricants; Lewkowitsch, Chemical Technology of Oils, Fats, and Waxes; Redwood, Lubricants, Oils, and Greases; G. H. Hurst, Lubricating Oils, Fats, and Greases; Carpenter and Leask, Soap, Candles, Lubricants, and Glycerin, 258 *et seq.*; Discussion on Lubrication, Phy. Soc. of London, 1919, 32, 15; J. Soc. Chem. Ind. 1919, 38, 7T; Archbutt, J. Soc. Chem. Ind. 1921, 40, 287T; Report Lubrication Inquiry Committee, 1920 (Dept. of Scient. and Indust. Research).

LUCERNE or **ALFALFA.** *Medicago sativa* (Linn.). A leguminous plant bearing loose racemes of bluish-purple flowers. Its root penetrates very deeply into the soil and thus enables it to sustain drought. It is chiefly used as a fodder plant for horses, cattle and sheep, being generally cut and eaten green, though sometimes made into hay. It should be cut at or before the flowering period, or it tends to become woody and less digestible. The following shows the average composition of the plant in the freshly cut condition:—

	Water	Proteids	Amino compounds	Carbo-hydrates	Fat	Fibre	Ash
Very young .	81·1	4·0	1·6	6·2	0·8	4·4	1·9
Before flowering . .	76·0	3·0	1·5	9·6	0·8	6·8	2·3
In full flower .	76·0	2·7	1·2	9·3	0·8	7·8	2·2

While the hay from the plant has the composition:

Cut before flowering .	16·0	12·2	4·0	31·1	2·4	27·0	7·3
Cut in flower .	16·5	10·7	3·5	29·2	2·6	29·5	8·0

The ash is rich in lime. Lucerne hay has marked diuretic properties. The seed is small and kidney-shaped, and is borne in a spiral pod. For a study of the enzymes present in various parts of the plant, see Jacobson and Holmes (J. Amer. Chem. Soc. 1914, 36, 2170; J. Chem. Soc. Abst. 1913, 1, 151, ; 1914, 1, 1193). For lucerne-seed oil, *see* J. and H. (J. Amer. Chem. Soc. 1916, 38, 480).

The ash of lucerne contains:

K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl
25·3	1·1	5·8	48·0	8·5	6·1	2·0	1·9

H. I.

LUCIDOL. Trade name for benzoyl peroxide used as an oxidising agent. Is a powerful antiseptic and may be employed as a drier towards linseed oil and other drying oils and for bleaching oils. Explodes on heating.

LUCIFERESCEINE. The fluorescent material present in certain luminous insects, particularly the fireflies (*Photinus pyralis*), (*P. corruscus*) and (*P. scintillans*). An alcoholic solution of the sticky fluid which the insects emit when irritated, has a bright blue fluorescence, yields a pale yellow amorphous substance, *luciferesceine*, giving a red coloration with concentrated sulphuric acid, and a dense cream-coloured precipitate with potassium ferrocyanide (Coblentz, Physikal. Zeitsch. 1909, 10, 955; McDermott, J. Amer. Chem. Soc. 1911, 33, 410).

LUDYL. Phenyl-disulphaminotetra-dioxy-diamino-arseno-benzene.

LUMINAL. Trade name for phenylethyl barbituric acid $C_6H_5 \cdot C \cdot C_2H_5[CO \cdot NH]_2CO$ now officially termed 'phenylbarbital' in America (*v.* PYRIMIDINES AND SYNTHETIC DRUGS).

LUMINAL-SODIUM. The sodium salt of phenylethylbarbituric acid. A white hygroscopic powder, readily soluble in water and alcohol, sparingly soluble in ether and chloroform

On boiling the solution, the salt is decomposed with evolution of carbon dioxide and formation of phenyl ethyl acetyl urea.

LUMINOUS PAINT *v.* BARIUM SULPHIDE.

LUMINOUS PAINTS, MANUFACTURE OF. Four methods for the manufacture of phosphorescent pigments are employed. The first utilises oyster shells as the raw material. The shells are first washed with hot water and then dried and calcined at a bright red heat. After cooling, the mass is crushed and freed from the *débris* of the external layers. The shell powder is then mixed with a small amount of powdered wood charcoal and transferred to a clay crucible, where it is arranged in alternate layers with powdered sulphur. The crucible, covered by a lid securely luted on, is strongly heated for about an hour, and after cooling the mass is extracted and pulverised. A phosphorescent colour prepared in this way from an impure calcium carbonate affords a more intense light than the colours made from pure carbonate of lime. In the second method the sulphates of calcium, barium, or strontium are used as the raw materials. These are intimately mixed with powdered wood charcoal, in the proportions of 1 part of carbon to 5 or 6 parts of sulphate. The mixture is then calcined as in the previous process. In the third method, when working with carbonates such as marble, witherite, or carbonate of strontium it is necessary to add, in addition to the wood charcoal, rather more than one chemical equivalent of sulphur, and then to proceed in the same manner as with the oyster shells. The second and third processes give masses with an orange, green, blue, or red phosphorescence. The sulphur is sometimes replaced by antimony sulphide or other similar sulphur compounds. More luminous but more expensive colours can be produced by starting with calcium oxide, barium carbonate, or carbonate or sulphate of strontium, either alone or mixed with calcium oxide or marble. The necessary carbon is obtained from starch, which is mixed with the above substances. The carbonates of rubidium and lithium, as well as bismuth nitrate, are equally of service. Sometimes sodium sulphate, or even lead acetate, is added, and the formulæ for the mixings vary with each individual factory. It may be taken as a general rule, however, that about 80 parts of the principal constituent require 12 parts of sulphur (or less if other sulphur compounds be present); 4 to 5 parts of starch, 2 to 4 parts of lithium carbonate, and 0·01 to 0·5 part of other metallic compounds. Those constituents, which are used only in very small amounts, are best added in alcoholic solution. The mixtures are heated in a closed crucible for three-quarters to one hour at a temperature of about 1200°C. Phosphorescent pigments are, when used, often mixed with barium sulphate, lakes of natural colouring matters, and often with mineral pigments of the same shade as the phosphorescent body itself. Thus, for example, realgar is used with red shades and orpiment with yellow shades (O. Prager, Chem. Tech. Fabrikant, through Chem. Trade Journ. August 6, 1921, 158).

LUNAR CAUSTIC. Silver nitrate fused and cast into rods or sticks.

LUPANINE $C_{15}H_{24}ON_2$ occurs in the *d-* and *dl-* form in the seeds of *Lupinus albus* (Linn.), and in the *d-* form in those of *L. angustifolius* (Linn.) and *L. perennis* (Linn.). The *dl-* form crystallises in needles, m.p. 99°, and furnishes crystalline salts. The *d-* form has m.p. 44°, and yields salts which are less soluble and crystallise more easily than those of the *dl-* form. The *l-* form, which may be separated from racemic lupanine, has m.p. 43°-44°, and crystallises less easily than the *d-* form. It has been suggested from time to time that lupanine is closely related to sparteine, but according to Beckel (Arch. Pharm. 1911, 249, 329; 1912, 250, 700), this is not the case. All the forms of lupanine are bitter and poisonous (Eichhorn, Nobbes Vers. St. 1867, 272; Siebert, Chem. Soc. Abstr. 1892, 62, 223; Soldaini, Boll. Chem. Farm. 1902, 41, 37, Arch. Pharm. 1902, 240, 260; Davis, Apoth. Zeit. 1896, 11, 94).

LUPEOL. A substance of the formula $C_{30}H_{50}O$ found associated with cinnamic acid in *Palaquium* [*Dichopsis*] *Treubii* (Burck.). Crystallises in fine needles, dextrorotatory $a_D = +27{\cdot}2°$ in chloroform, m.p. 190°-192° (Jungfleisch and Leroux, Compt. rend. 1907, 144, 1435; *cf.* Van. Romburgh, *ibid.* 1907, 926).

LUPINES. *Lupinus luteus* (Linn.); *L. angustifolius* (Linn.); *L. albus* (Linn.). The above three varieties, whose flowers are yellow, blue, and white respectively, are the chief species grown. They are often grown for green manure on account of their nitrogen-collecting powers, and are employed to enrich poor sandy soils in nitrogenous organic matter. They are only occasionally used as food either for men or animals, because of their bitter taste, but in times of famine they are sometimes used as an addition to rye-bread.

The following gives the mean composition of several varieties of the seed (Konig):—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
White lupines	15·9	28·8	6·8	33·6	11·9	3·0
Black ,, .	14·3	38·8	4·6	23·9	14·5	3·9
Blue ,, .	14·3	29·7	5·3	35·6	12·2	2·9
Yellow ,, .	14·7	37·8	4·3	25·5	14·2	3·5

The 'protein' of lupines contains a considerable proportion (10–20 p.c.) of non-albuminoids. A portion of the non-albuminoid nitrogen exists in the form of alkaloid-like substances. Blue and white lupines contain a substance *lupanin* $C_{15}H_{24}N_2O$, which can exist in two forms: a liquid which forms a hydrochloride $C_{15}H_{24}N_2O.HCl,2H_2O$, crystallising in prisms melting at 132°-133°; and a solid, crystallising in monoclinic crystals, which melt at 99°, and which forms a hydrochloride of the same composition as the other, but melting at 105°-106°. *Lupinin* $C_{21}H_{38}N_2(OH)_2$ occurs in yellow lupines; it forms crystals melting at 67°-68°. *Lupinidin*, another liquid alkaloid-like substance, consists of a solution of a crystalline hydrate $C_8H_{15}N+H_2O$ in the oily base $C_8H_{15}N$. The latter is a thick, oily liquid easily soluble in alcohol and ether, smells like hemlock and has an intensely bitter taste. It oxidises rapidly by exposure to air and acts as a weak poison.

These alkaloid-like substances are present both in the seeds and in the leaves and stems, and thus render the plant unpalatable to animals. The poisonous properties of lupines, often fatal to sheep, were formerly ascribed to these alkaloids, but according to Kuhn and Liebscher, they are due to 'Ichtrogen,' a substance produced by the growth of a fungus which attacks lupines, and which can be extracted from diseased plants by treatment with water.

Lupines are sometimes deprived of their bitter taste before being given to animals. This can be done by an hour's steaming and washing with water; according to Kellner this treatment removes practically the whole of the alkaloids (95 p.c.), while it also removes about 3-4 p.c. of the nitrogenous substances, and 15–20 p.c. of the total dry matter. In spite of this loss the treated lupines are of greater feeding value than those untreated.

Of the proteids in lupines, conglutin is the largest constituent. The 'nitrogen free extract' of lupines consists largely of gums and pectin bodies, together with starch and cane sugar. The blue lupine contains about 11 p.c. of *lupeose* (*β*-galactan): by heating with dilute sulphuric acid it splits up into *d*-fructose and galactose.

The following are analyses of the ash of lupines (König):—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Yellow lupines	30·5	0·7	7·1	12·8	0·7	38·6	8·7	0·2	0·8
Blue ,,	30·9	1·0	10·6	9·7	0·6	37·1	7·8	1·0	0·4
White ,,	33·7	17·9	7·8	6·2	—	25·7	6·8	0·9	2·1

H. I.

LUPINIDINE (*Sparteine*) *v.* BROOM TOPS.

LUPININE $C_{10}H_{19}ON$, an alkaloid found with sparteine in the seeds of *Lupinus luteus* (Linn.) and *L. niger*. Rhombic crystals, m.p. 67°–68°. Distils without decomposition in hydrogen at 225°–257°, lævorotatory. It is bitter and slightly toxic. Is a tertiary, hydroxy base which furnishes crystalline salts (Baumert, Ber. 1881, 14, 1150; 1882, 15, 1951; Hagen, Annalen, 1885, 230, 370; Siebert, Arch. Pharm. 1891, 229, 531; Soldaini, *ibid.* 1892, 230, 16; Berend, *ibid.* 1897, 235, 262; Willstatter and Fourneau Ber. 1902, 35, 1910).

LUPULIN *v.* OLEO-RESINS.

LUTECIENNE. A mixture of Fast Red A with Orange II. (*β* naphthol orange), the sodium salt of *p*-sulphobenzene-azo-*β*-naphthol, comes into commerce under this name. Known also as French Red. The name is also given to the alkaline salts of dibromodinitro-fluorescein, prepared by simultaneous nitration and bromination of fluorescein in alcoholic solution or by nitration of dibromofluorescein in acetic acid or aqueous solution.

LUTECIUM. Sym. Lu. At.wt. 174 (175·0 Auer von Welsbach). The identification of this rare earth metal has resulted from the systematic examination of Marignac's ytterbia (Compt. rend. 1878, 87, 578), which is isolated from the least basic portions of the yttria earths derived from xenotime or ytterbite (gadolinite) (*v.* CERITE METALS). Prolonged fractionation in nitric acid of the crude ytterbium nitrate removed yttrium, erbium, and finally thulium, a trace of thorium being separated with hydrogen peroxide. The atomic weight of the elements present in the final fractions rose from 169·9 to 173·8. The most soluble fractions, which give the highest atomic weights, showed 34 characteristic lines in the spark spectrum and the band *γ* (λ517·5–λ513) in the absorption spectrum which are characteristic of lutecium (Urbain, Compt. rend. 1907, 145, 759; *cf.* Auer von Welsbach, Sitzungsber. Wien. Akad. 1907, 468). The commercially separated yttrium earths from ytterbite have been further fractionated as chromates to remove yttrium, and crystallised as nitrates, and as double nitrates with bismuth and magnesium to precipitate cerium and lanthanum. After removing the excess of bismuth and magnesium, the lutecium fraction was precipitated as oxalate, converted into nitrate, and fractionated to eliminate successively erbium, yttrium and neoytterbium. The most soluble lutecium fraction, converted into chloride with sulphur chloride (*v.* CERIUM), was heated till scandium and thorium chlorides were volatilised. *Lutecium chloride* is more volatile than neoytterbium chloride (Urbain, Bourion, and Maillard, Compt. rend. 1909, 149, 127). The xenotime earths were freed from cerium, gadolinium, terbium and dysprosium by fractionating the ethyl sulphates; the most soluble ytterbium fraction (containing yttrium, erbium, and thulium) was converted into nitrate, and decomposed fractionally in nitric acid when neoytterbium and lutecium were obtained in the most easily decomposable portions (*cf.* Auer von Welsbach, Monatsh. 1913, 34, 1713).

Lutecia (*lutecium oxide*) Lu_2O_3 is less basic than neoytterbia, and can be separated from it by fractional precipitation with caustic alkali; it is less paramagnetic than the latter oxide, the magnetic susceptibilities being in the ratio $Yb_2O_3 : Lu_2O_3 = 53 : 13$ (Urbain, Compt. rend. 1908, 146, 406).

The final uncrystallisable mother liquors obtained in the separation of lutecium from ytterbite (but not from xenotime) probably contain a new element *Celtium* indicated by a characteristic arc spectrum. The magnetic susceptibility of celtium oxide is three or four times less than that of lutecia, and in basic strength the former oxide is intermediate between the latter and scandia (Urbain, Compt. rend. 1911, 152, 141; Urbain and Blumenfeld, *ibid.* 1914, 159, 323) (*v.* CELTIUM). G. T. M.

LUTEOLIN. The sodium salt of *m*-xylidinsulphonic-azo-diphenylamine. An orange-yellow dye discovered by Witt in 1883. No longer used. Also the colouring matter of weld (*q.v.*).

LUTES are used for packing joints, repairing fractures, and coating vessels externally to render them impervious to vapours, &c. For a lute to be effective it is important that the surfaces to which it is applied should be *clean*, and in the case of lutes that are applied in a molten or semi-fluid state it is preferable previously to heat the parts that are to be joined.

Of lutes for joints which are not to be subjected to high temperature may be mentioned: (1) Soaked bladder stretched and tied over a joint or employed to secure another lute on the joint. (2) India-rubber bands, or caoutchouc melted or dissolved in coal tar, naphtha, or other solvent. (3) A solution of 1 part caoutchouc in 2 parts hot linseed oil mixed with 3 parts pipeclay; this mixture remains soft and is very impervious. (4) Linseed or almond meal made into a paste with water, milk, glue, or lime-water. (5) A mixture of white lead and oil spread upon strips of linen or bundles of tow. (6) Quicklime reduced to a dry powder by addition of a small quantity of water, and mixed with white of egg diluted with its own volume of water, is spread on linen strips and rapidly applied to the joint. This lute dries quickly and adheres strongly to glass. (7) *Lute d'âne*, a very strong cement prepared by mixing strong glue with recently slaked lime, with subsequent addition of white of egg. (8) Chalk and linseed oil (glazier's putty). (9) Plaster of Paris made into a paste with water, gum water, or glue, and coated when dry, if the joint is to be gas-tight, with melted paraffin or oil. (10) *Fat lute*, consisting of a mixture of clay and boiled linseed oil, is applied and retained by bladder or other substance, to hot joints or to prevent escape of corrosive vapours. (11) A mixture of clay with a solution of gelatin in pyroligneous acid.

For joints which are to resist considerable internal pressure, especially the joints of steam pipes, a mixture is applied consisting of equal parts of red lead and white lead made into a paste with linseed oil and mixed with tow. Other lutes for this purpose are: (1) 12 of Paris white, 5 of red ochre, 2½ of Venetian red, and ½ of plumbago, ground and mixed to a stiff paste with boiled linseed oil (Thompson, Eng. Pat. 27975, 1895). (2) Metallic zinc powder mixed with tow or whiting and made into a paste with linseed oil or wood oil (Boneville & Co. Fr. Pat. 332788). (3) 6 parts graphite, 3 parts slaked lime, 8 parts powdered barytes, and 7 parts of boiled linseed oil.

For making permanent joints and closing joints between metal and glass, &c., various compositions containing beeswax are used. Beeswax when melted with one-eighth its weight of turpentine becomes less brittle and, when the materials are melted in equal proportions, the product becomes pliant when held in the hand, melts easily, and is known as *soft cement*. *Cap cement* or *hard cement*, for closing the covers, &c., of scientific apparatus, is prepared by mixing and melting 1 part beeswax, 5 parts resin, and 1 part dried red ochre or other colouring matter. The mixture is heated to 100°C. until all frothing has ceased, and is cooled with frequent stirring to prevent settlement of the pigment.

Bottle lutes are used to cover the stoppers or corks of bottles. That most commonly employed is sealing wax; paraffin wax is also good. Wholesale dealers usually lute the stoppers of acid bottles with a paste of linseed meal and water.

Plumber's lute is made by adding 2 parts of fine brickdust to 1 part of melted black resin and stirring in thoroughly.

A *waterproof cement*, introduced by Edmund Davy, is prepared by melting together 2 parts by weight of common *pitch* and 1 part of *gutta percha*, with constant stirring. The resultant homogeneous fluid adheres with great tenacity to metal, stone, wood, &c., if applied to warm surfaces of those substances, and, although hard, is not brittle. It softens when heated and passes through various stages of viscosity until above 100°F. it forms a thin fluid. It appears to be absolutely unaffected by contact with water.

Mixtures of boiled linseed oil, clay, asbestos and red or white lead are waterproof, as is a mixture of flax seed meal and water. Portland cement mixed with water containing sodium silicate or glue makes a good lute.

Oil proof cements may be made from (*a*) glue, glycerol and water; (*b*) molasses and flour; (*c*) sodium silicate and whiting, or barium sulphate.

Two good *acid-proof* lutes are: (1) Pipeclay made into a stiff paste with hot coal-tar; (2) equal parts of pitch and resin melted together and incorporated with 1 part of plaster of Paris; (3) equal weights of rubber (dissolved in CS_2) and boiled linseed oil.

A useful laboratory cement is obtained by mixing litharge to a stiff paste with glycerol. This quickly sets to a hard mass, impervious to water or gases.

This cement is employed for lining the digesters used in the manufacture of sulphite pulp. For its behaviour in setting, *see* Merwin, J. Ind. Eng. Chem. 1917, 9, 390. A suitable mixture for joints of silica ware (vitreosil) consists of 40 parts of asbestos, small, 8 parts asbestos fibre, 10 parts whiting, 2–3 parts tallow, boiled linseed oil 39–40 parts.

A *chlorine resistant cement* consists of powdered glass (1), Portland cement (1), sodium silicate (1).

Acetone collodion, a solution of collodion in acetone, is very useful as a lute in the laboratory. Painted on with a brush, it quickly dries to a hard film, which is proof against water and dilute acids, and is perfectly impervious to gases. It may be used to lute cork or rubber stoppers, to cover rubber tubing, to waterproof labels, &c., but it should not be subjected to a temperature above 150°C.

A lute acquiring a hardness equal to that of marble, and known as *oxychloride of zinc cement* (Sorel's cement), is prepared by dissolving 3 p.c. of borax in a solution of zinc chloride of 1·49–1·65 sp. gr. with addition of sufficient recently ignited zinc oxide to produce the proper consistency.

Magnesia cement is prepared by making a paste of powdered magnesite and 10–20 p.c. conc. hydrochloric acid, forming it into blocks, igniting, and finally grinding to powder. With water this yields a strong cement which quickly sets hard, but is not absolutely fireproof.

Bruyère's hydraulic cement is prepared by heating to bright redness for 3 hours a mixture of 3 parts clay and 1 part slaked lime, and powdering the product.

A cement employed for closing leaks in boilers, &c., is prepared by mixing 6 parts clay and 1 part iron filings to a paste with boiled linseed oil.

Iron cement, for permanently closing joints in iron, consists of a mixture of 100 parts iron filings, 3–20 parts flowers of sulphur, and 3–5 parts ammonium chloride, mixed with water to a paste and applied quickly. The larger proportion of sulphur is required when the iron filings are fine. The mixture soon becomes hot, with evolution of ammonia and sulphuretted hydrogen, and in a short time becomes almost as hard as iron. It is stated that the best iron lute consists of a mixture of 100 parts iron filings with only 1 or 2 parts of sal ammoniac and no sulphur. This lute, however, though stronger, requires a considerable time to set.

For coating earthenware, a paste is applied consisting of a mixture of equal parts of zinc white and fine sand, made into a paste with a concentrated solution of zinc chloride. *Willis' lute* for the same purpose consists of a paste made with slaked lime and a solution of 2 oz. borax in 1 pint water. It is applied with a brush, and when dry is covered with a plastic mixture of slaked lime and linseed oil and is ready for use after a few days.

Among lutes for resisting high temperatures may be mentioned Stourbridge clay made into a paste with water, which withstands a higher temperature than any other lute in general use, and *Windsor loam*, a natural mixture of clay and sand. Both are used for coating vessels and for packing hot joints of metal vessels. With the addition of about one-tenth part of borax these clays are useful for glazing earthenware vessels. Leaks and fractures in furnace linings, &c., may be stopped with *ganister*, a highly siliceous fireclay.

Gas retorts and similar vessels closed temporarily to withstand high temperatures are usually merely luted with mortar.

For luting crucibles, a paste of fireclay and powdered firebrick is useful, preferably with addition of a small proportion of borax to render the lute coherent.

A most valuable mixture for repairing broken furnaces, &c., consists of a paste of firebrick and liquid sodium silicate. Even considerable openings, if roughly filled with broken firebricks, may be sealed with this lute.

A fireproof cement for repairing retorts, &c., is made by taking 200 cwt. china clay, 100 cwt. barytes, 40 gall. sodium silicate (100 Tw.), 24 gall. water, and 28 lbs. borax, mixing well and adding magnesite to the extent of 25 p.c. of the mixture (Williams, Eng. Pat. 18064, 1903).

A lining for furnaces and crucibles may be made from 4 parts granular corundum, ground to a fine powder, mixed with 1 part powdered graphite and made into a paste with 10 p c. of sodium silicate (Crowley and Payne, Eng. Pat. 8627, 1906; *v.* also Kilburn Scott, J. Soc. Chem. Ind. 1905, 501).

For other recipes *see* Sadtler, Chem. News, 1916, 113, 257; Analyst, 1916, 262.

LUTIDINES, LUTIDINIC ACID *v.* BONE-OIL.

LYCACONITINE *v.* ACONITINE.

LYCETOL. *See* Lysetol.

LYCIN (Acidol). Trade name for betaine hydrochloride.

LYCOPERDON GEMMATUM. According to Kotake and Naito (Zeitsch. physiol. Chem. 1914, 90, 254) the fungus *Lycoperdon gemmatum* on extraction with alcohol gives a crystalline brown dyestuff. This is a glucoside, and when hydrolysed gives dextrose and *gemmatein* $C_{17}H_{12}O_7$, brown needles. Fusion with alkali gives *p-hydroxyphenylacetic acid*, and when oxidised with hydrogen peroxide *homogentisic anhydride* is produced.

LYCOPODINE, $C_{32}H_{52}O_3N_2$, m.p. 114°–115°, is a crystalline alkaloid of bitter taste, occurring in *Lycopodium complanatum* (Boedeker, Annalen, 1881, 208, 363). In *Lycopodium Saururus* of tropical S. America there occurs *pillijanine* $C_{15}H_{24}ON_2$ crystals m.p. 64°–65°, with an odour of conine (Arata and Canzoneri, Gazz. 1892, 22, 1, 146). These two alkaloids, with those in ergot, are the only known alkaloids in Cryptogams. G. B

LYCORINE $C_{32}H_{32}O_8N_2$ occurs in the bulbs of *Lycoris radiata* (=*Nerine japonica*) and forms large crystals, m.p. 250° (Morishima, Arch. exp. Path. Pharm. 1897, 40, 221) It has an emetic action. The bulbs contain a second crystalline alkaloid *sekisanine* $C_{34}H_{36}O_9N_2$. G. B.

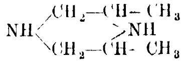
LYDDITE *v.* EXPLOSIVES.

LYDIAN STONE or **LYDITE** (*Lapis Lydius*, of Pliny, from Lydia, in Asia Minor). A black, jaspideous or cherty variety of quartz, which from its hardness and the closeness of its grain has been used as a touchstone for testing the quality of gold, whence its name *basanite*. The metal to be tested is rubbed on the polished surface of the stone, and the streak thus produced is compared with the streaks made by a series of alloys of known composition; the observer judging of the purity of the metal by the colour of the mark and by its behaviour when treated with a drop of acid. Lydite is also used as a hone-stone. Most Lydian stone has a schistose structure, and may be described as a hornstone-slate, or *Kieselschiefer*. The Lydian stone of Devon and east Cornwall is a fine-grained, indurated, carbonaceous shale, belonging to the Culm-measures. In Fifeshire it is represented by blocks of baked shale in the vents of ancient volcanoes. L. J. S.

LYDIN. A synonym for mauve or aniline purple.

LYGOSIN. Trade name for di-hydroxydibenzalacetone.

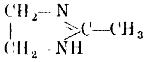
LYSETOL. Trade name for the tartrate of of dimethylpiperazine



$$NH\left\langle\begin{matrix}CH_2—CH—CH_3\\ \\ CH_2—CH—CH_3\end{matrix}\right\rangle NH$$

used as a uric acid solvent.

LYSIDIN. Ethylene-ethenyl-diamino



$$\begin{matrix}CH_2—N\\ |\\ CH_2—NH\end{matrix}\rangle C—CH_3$$

Prepared by heating sodium acetate and ethylene diamine hydrochloride. Used as a uric acid solvent.

LYSINE $NH_2[CH_2]_4CH(NH_2)CO_2H$, *$\alpha\epsilon$-diaminohexoic acid*, was discovered by Dreschel (J. pr. Chem. 1889, [ii.] 39, 425; *see*, also, van Slyke, J. Biol. Chem. 1913–14, 16, 531; and Funk and McLeod, Biochem. J. 1914, 8, 109) among the products of hydrolysis of casein by hydrochloric acid and stannous chloride; it is produced by the hydrolysis of other proteins, conglutin, egg albumen, fibrin (Siegfried, Ber. 1891, 24, 418), and gelatin (Ernst Fischer, Arch. Anat. u. Physiol. 1891, 265; Osborne and Leavensworth, J. Biol. Chem. 1913, 14, 481; *cf.* van Slyke and Birchard, *ibid.* 1914, 16, 539); it occurs in antipeptone prepared from fibrin (Kutscher, Zeitsch. physiol. Chem. 1898, 25, 195); together with arginine it forms the chief product of hydrolysis of the protamines sturine, β-cyprinine, and crenilabrine (Kossel, Zeitsch. physiol. Chem. 1899, 26, 588; 1904, 40, 565; 1910, 69, 138; it also occurs among the hydrolytic products of the proteins of the seeds of various conifers, and the seedlings of *Lupinus luteus* (Linn.) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1899, 28, 459, 465; 1901, 33, 547), and has been found in *Shiokara*, Suzuki Yoneyama (J. Col. Agric. Tokyo, 1912, 5, 33), and in fungi (Reed, J. Biol. Chem. 1914, 19, 257); Omeliansky and Sieber (Zeitsch. physiol. Chem. 1913, 88, 445).

Dreschel (Chem. Zentr. 1891, ii. 712) showed that lysine is a diaminocaproic acid, and Ellinger (Ber. 1899, 32, 3542) proved that the two amino groups are in the *αε*- positions, because on decomposition by putrefaction in an atmosphere of hydrogen, lysine is partially converted into cadaverine (pentamethylenediamine)

$$\mathrm{NH_2[CH_2]_4CH(NH_2)CO_2H} = \mathrm{CO_2} + \mathrm{NH_2[CH_2]_5NH_2}$$

cf. Ackermann (Zeitsch. physiol. Chem. 1910, 69, 273). The synthesis of *i*-lysine has been effected by Fischer and Weigert (Sitzungsber. K. Akad. Wiss. Berlin, 1902, 270) from ethyl *γ*-cyanopropylmalonate; when this compound is treated with ethyl nitrite it gives ethyl *α*-oximino *δ*-cyanovalerate $\mathrm{CN[CH_2]_3C(NOH)CO_2Et}$, which on reduction with sodium in alcoholic solution, yields *αε*-diaminohexoic acid or *i*-lysine

$$\mathrm{NH_2[CH_2]_4CH(NH_2)CO_2H},$$

this is isolated by successive transformation into the phosphotungstate and picrate; the *picrate* forms thick needles that darken at 230°; the *hydrochloride* is crystalline and melts at 183°-186° (corr.); the *phenylcarbimide* forms colourless needles, m.p. 182°-185° (corr.); these derivatives differ from the corresponding derivatives of the naturally occurring *d*-lysine in being optically inactive and having slightly different melting-points. A further synthesis of *i*-lysine from ethyl cyanopropylphthaliminomalonate is described by Sorensen (Chem. Zentr. 1903, ii. 33); when this compound is reduced with sodium in alcoholic solution it yields the corresponding amino compound

$$\mathrm{C_6H_4:(CO)_2:N{\cdot}C(CO_2Et)_2[CH_2]_3NH_2},$$

which is transformed by the action of concentrated hydrochloric acid into *i*-*αε*-diaminohexoic acid (*i*-lysine)

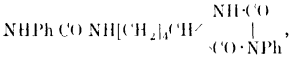
i-Lysine can also be obtained by a synthetic process from piperidine (Julius von Braun, Ber. 1909, 42, 839). The opening of the piperidine ring by phosphorus pentachloride affords among other products, benzoyl-*ε*-leucinenitrile $\mathrm{COPh{\cdot}NH[CH_2]_5CN}$, which contains the skeleton of lysine, and yields on hydrolysis *ε*-benzoylaminohexoic acid $\mathrm{COPh{\cdot}NH[CH_2]_5CO_2H}$; this on bromination forms the *α*-bromo derivative $\mathrm{COPh{\cdot}NH[CH_2]_4CHBr{\cdot}CO_2H}$, which reacts with ammonia to give *α*-amino-*ε*-benzoylaminohexoic acid $\mathrm{COPh{\cdot}NH[CH_2]_4CH(NH_2)CO_2H}$, from which *i*-lysine is obtained by hydrolysis.

Derivatives. *Salts.*—*d*-Lysine is a syrup (Winterstein, Zeitsch. physiol. Chem. 1905, 45, 77), it has $[\alpha]_D + 17{\cdot}5°$ in hydrochloric acid solution (Lawroff, *ibid.* 1899, 28, 388), and forms well-defined crystalline salts and double salts; the *monohydrochloride* is strongly acid, the *dihydrochloride* is a neutral substance (Dreschel, Arch. Physiol. 1891, 248); the *platinichloride* $\mathrm{C_6H_{14}O_2N_2{\cdot}H_2PtCl_6{\cdot}EtOH}$ crystallises with 1 molecule of alcohol which it loses at 120°; *i-lysine platinichloride* has the composition $\mathrm{C_6H_{14}O_2N_2{\cdot}H_2PtCl_6}$, it crystallises in prisms of a paler yellow colour than those of active lysine platinochloride. Siegfried (Zeitsch. physiol. Chem. 1912, 76, 234); the *aurichloride*

$$\mathrm{C_{12}H_{28}O_4N_4{\cdot}HCl{\cdot}3HAuCl_4,2H_2O}$$

sinters at 120° and melts at 152°-155°; *i-lysine aurichloride* $\mathrm{C_{12}H_{28}O_4N_4{\cdot}4HAuCl_4,H_2O}$ decomposes at 173°-176° (Siegfried, Zeitsch. physiol. Chem. 1905, 43, 363; Ackermann, *ibid.* 1908, 56, 305); the *picrate* $\mathrm{C_6H_{14}O_2N_2{\cdot}C_6H_3N_3O_7}$ is sparingly soluble in alcohol (Kossel, Zeitsch. physiol Chem. 1899, 26, 586), and advantage is taken of this fact in the quantitative separation of lysine from arginine and histidine (Kossel and Kutscher, *ibid.* 1900, 31, 165; Kossel and Weiss, *ibid.* 1910, 68, 165; Schreiner and Shorey, J. Biol Chem. 1910, 8, 381) Lysine phosphotungstate crystallises in anhydrous needles, Drummond (Biochem. J. 1918, 12, 5); *see* Wechsler, Zeitsch. physiol. Chem. 1911, 73, 138, for the solubility of the phosphotungstate precipitate in a mixture of acetone and water.

Lysine readily yields an additive product with phenyl*iso*cyanate, this does not crystallise well, but on treatment with concentrated hydrochloric acid is converted into the *hydantoin*



$$\mathrm{NHPh{\cdot}CO{\cdot}NH[CH_2]_4CH}\begin{cases}\mathrm{NH{\cdot}CO} \\ \quad | \\ \mathrm{CO{\cdot}NPh}\end{cases}$$

, which is crystalline and melts at 183°-184° (Herzog, Zeitsch. physiol. Chem. 1902, 34, 525), the corresponding derivative of *i*-lysine has m.p. 156° (von Braun, Ber 1909, 42, 839).

Lysuric acid, the dibenzoyl derivative of lysine, has m.p. 144°-145°; the *acid barium salt*

$$2(\mathrm{C_6H_{12}Bz_2N_2O_2}),(\mathrm{C_6H_{11}Bz_2N_2O_2})_2\mathrm{Ba,2H_2O}$$

crystallises in beautiful needles, m.p. 144°-148°, at which temperature it becomes anhydrous; the *normal barium salt* $\mathrm{(C_{20}H_{21}N_2O_4)_2Ba,1\tfrac{1}{2}H_2O}$ is a white crystalline powder, m.p. 168°; the *acid sodium salt* is white and crystalline, m.p. 108°-109°, and contains $\mathrm{H_2O}$; the *acid strontium salt* contains $\mathrm{2H_2O}$, crystallises in plates, and has m.p. 137°-138°; the *normal strontium salt* contains $\mathrm{H_2O}$ and is crystalline; the silver salt $\mathrm{C_{20}H_{21}N_2O_4Ag,1\tfrac{1}{2}H_2O}$ is white and amorphous (Dreschel, Ber. 1895, 28, 3189; Willdenow, Zeitsch. physiol. Chem. 1898, 25, 523).

Methyl lysine hydrochloride prepared by the action of methyl alcohol and hydrogen chloride on *i*-lysine hydrochloride, has m.p. 218° (decomp.), *cf.* Engeland and Kutscher (Zeitsch. Biol. 1912, 59, 415); *lysine anhydride*, obtained by heating the methyl ester at 100°, forms the *picrate* $\mathrm{C_{12}H_{24}O_2N_4{\cdot}2C_6H_3O_7N_3}$ yellow prisms or plates decomposing at 230° (corr.), and the *hydrochloride*, microscopic colourless needles decomposing at 270° (corr.) (Fischer and Suzuki, Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1333). *d-Lysyl-lysine dipicrate*

$$\mathrm{C_{12}H_{26}O_3N_4,(C_6H_3O_7N_3)_2},$$

m.p. 238°-242° was isolated from the products of hydrolysis of pepsin extract (Hugounenq and Morel, Compt. rend. 1909, 148, 236); *i-lysyl-lysine* $\mathrm{C_{12}H_{26}O_3N_4}$ forms a yellow crystalline *picrate*, m.p. 185° (corr.), and a *hydrochloride* crystallising in short twin prisms, m.p. 205° (corr.) (Fischer and Suzuki, Ber. 1905, 38, 4173).

Lysine yields carbamide when decomposed by barium hydroxide (Dreschel, Ber. 1890, 23, 3096); it is oxidised by barium permanganate, yielding glutaric acid as the chief product (Zickgraf, Ber. 1902, 35, 3401); and when the sulphate or hydrochloride is treated with barium or silver nitrite, αε-dihydroxyhexoic acid, an aminohydroxyhexoic acid, m.p. 200°–201°, and a small amount of an alkaline yellow amorphous substance $C_8H_{13}O_3N$, m.p 176°-178°, are produced (Szydlowski, Monatsh. 1906, 27, 821). Heated with nitrous acid above a temperature of 30° all the nitrogen is set free from lysine in ten minutes (Sure and Hart, J. Biol. Chem. 1917, 31, 527).

Experiments made by Buckner, Nollau and Kastle (Amer J. Physiol. 1915, 39, 162) support the view that lysine is largely responsible for the stimulation of growth; Osborne and Mendel (J. Biol. Chem. 1916, 25, 1) point out the necessity of the presence of a certain proportion of lysine in order to form a nitrogen food suitable for producing satisfactory growth. *Cf.* Lewis and Root (J. Biol. Chem. 1920, 43, 79). *Cf.*, however, McCallum, Simmonds and Smith (J. Biol. Chem. 1917, 28, 483; Abderhalden (Zeitsch. physiol. Chem. 1915, 96, 1–147).

Lysine possesses germicidal properties (Wagner, Zentralblatt F. Baktr. u. Parasit. 11, Abt. 42, 613). M. A. W.

LYSINE. This term is also used as a trade name for a preparation consisting of an acid solution of formalin containing inorganic salts and essences. Used as an antiseptic and bactericide.

LYSOCHLOR. Trade name for chloro-*m*-cresol.

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M

M ACID. 1-amino-5-naphthol-7-sulphonic acid.

MACARITE. An explosive consisting of a mixture of trinitrotoluene (30 parts) and lead nitrate (70 parts)

MACE. *Description.*—Mace is the dried arillus or seed coat of the nutmeg, the latter being the fruit of *Myristica fragrans* (Houtt.) (or *Myristica argentea* (Warb.), *see* below).

The tree is a native of the Malay Archipelago, and is cultivated in both the East and West Indies.

The fruit (nutmeg) is surrounded by four coats: a thick pericarp on the outside, then the crimson arillus, then a thick tegument, and finally a thin membrane closely adherent to the kernel.

Many other species of *Myristica* are known in addition to *M. fragrans* (Banda or true mace), but only one yields aromatic seeds, viz. *M. argentea*, which furnishes the Papuan or Macassar mace.

The chief varieties of mace which appear on the British market are Penang, Singapore, Java, and West Indian, the first being the most highly esteemed. All these are derived from *Myristica fragrans*, but a small quantity of Macassar mace is also imported, and this variety has hitherto been sold as "mace" without any question being raised as to its genuineness. As it appears in commerce, mace has a yellow-brown colour, the lighter the better. The arillus, when unbroken, is about 1½ inch long and ¾ inch wide at the base. It is usually flattened, the tapering segments or blades being from ⅛ to ¼ inch wide. Macassar mace is of a dull brown colour and has much wider blades. Both varieties have a similar aromatic flavour, but that of Macassar mace is distinctly acrid (*v.* Holmes, Pharm. J. 1908, 652). The sole use of mace is as a flavouring agent and condiment.

Composition.—The chief constituents of mace are a volatile oil to which the flavour is mainly due, a fixed oil and a carbohydrate, amylodextrin, the granules of which are easily visible under the microscope and turn red on treatment with iodine. The following table shows the composition of Banda and Macassar mace, and also of false or Bombay mace (*see* below).

(From Winton, Ogden and Mitchell, U.S. Dept. of Agric., Bul. 13 and 65, and other sources.)

			Ether extract				
	Water	Ash	Volatile oil	Fixed oil	Amylo-dextrin	Crude fibre	Nitrogen
Mace (*Myristica fragrans*)	5 67 to 12 04	1·62 to 4 10	4 04 to 10 80	21·20 to 29 08	22 60 to 31 60	2·90 to 8·90	0·73 to 1·12
Macassar mace .	4 18	2·01	5 89	53·50	10 40	4 57	1·11
Bombay mace	0 32 to 7 04	1 36 to 1 98	0·00 to 0·67	56·70 to 59·80	16·20	3·21 to 8 17	0 81 to 0 79

More recent analyses by Parry ('Food and Drugs,' p. 236) yielded the following figures:

	True mace	Macassar mace	Bombay mace
Total ash . . .	1 87 2 36	1·7–2·08	1·9–2·1
Do soluble in water .	1·08–1·27	1·1 1·25	1·0–1·2
Do. insoluble in HCl .	0 07–0 20	0 6–0 75	0·07–0 08
Fixed ether extract	25 0 32 5	49 5–52 0	58·0–63·0
Alcoholic extract .	22·0–25 0	38 0	45·8
Volatile oil . .	4·0–8 0	4·0–7·0	4 0–8·0
Fibre . . .	5·0–9·0	4 0–8 0	3 0–8·0
Nitrogen . . .	0·7–1·2	1·0–1 2	0·8–0 9
Ether extract after extracting with petroleum ether . .	2 0–3 5	similar to true mace	up to 33·0

Adulteration.—The only sophistication to which whole mace is liable is the addition of Bombay mace which is derived from *Myristica malabarica* (Lam.). The arillus of this species is about 2½ inches long by ¾ inch wide, and the numerous blades are narrow and their vermiform ends are coiled in a tangled mass at the apex. It is of a deep red-brown colour, and almost devoid of aroma. As it is quite useless as a flavouring agent, and its price is about one-fourth that of genuine mace, its presence in the latter can only serve the purposes of fraud.

Bombay mace is also the chief adulterant of ground mace, but potato, arrowroot, the cereal starches, turmeric, and ground olive stones may possibly be found.

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(From Winton, Ogden and Mitchell, U.S. Dept. of Agric., Bul. 13 and 65, and other sources.)

	Water	Ash	Ether extract		Amylodextrin	Crude fibre	Nitrogen
			Volatile oil	Fixed oil			
Mace (*Myristica fragrans*)	5·67 to 12·04	1·62 to 4·10	4·04 to 10·80	21·20 to 29·08	22·00 to 31·60	2·90 to 8·00	0·73 to 1·12
Macassar mace	4·18	2·01	5·80	53·50	10·40	4·57	1·11
Bombay mace	0·32 to 7·04	1·36 to 1·98	0·00 to 0·67	56·70 to 59·80	16·20	3·21 to 8·17	0·81 to 0·79

More recent analyses by Parry ('Food and Drugs,' p. 236) yielded the following figures:

	True mace	Macassar mace	Bombay mace
Total ash	1·87–2·36	1·7–2·08	1·9–2·1
Do. soluble in water	1·08–1·27	1·1–1·25	1·0–1·2
Do. insoluble in HCl	0·07–0·20	0·0–0·75	0·07–0·08
Fixed ether extract	25·0–32·5	49·5–52·0	58·0–63·0
Alcoholic extract	22·0–25·0	38·0	45·8
Volatile oil	4·0–8·0	4·0–7·0	4·0–8·0
Fibre	5·0–0·0	4·0–8·0	3·0–8·0
Nitrogen	0·7–1·2	1·0–1·2	0·8–0·9
Ether extract after extracting with petroleum ether	2·0–3·5	similar to true mace	up to 33·0

Adulteration.—The only sophistication to which whole mace is liable is the addition of Bombay mace which is derived from *Myristica malabarica* (Lam.). The arillus of this species is about 2½ inches long by ¾ inch wide, and the numerous blades are narrow and their vermiform ends are coiled in a tangled mass at the apex. It is of a deep red-brown colour, and almost devoid of aroma. As it is quite useless as a flavouring agent, and its price is about one-fourth that of genuine mace, its presence in the latter can only serve the purposes of fraud.

Bombay mace is also the chief adulterant of ground mace, but potato, arrowroot, the cereal starches, turmeric, and ground olive stones may possibly be found.

Detection of adulteration.—The presence of any of the above adulterants is best detected by means of the microscope. Banda and Macassar mace are practically indistinguishable from one another, but the presence of Bombay mace is at once revealed by the appearance of the dark orange-coloured oil cells, the contents of which when treated with alkali assume a blood-red tint. The oil cells in Banda and Papua mace are fewer in number, of a light yellow colour, and alter only slightly in appearance when treated with alkali. A further characteristic, which however can only be seen in transverse sections, is that the epidermal cells in Bombay mace are radially elongated whilst in the case of the other two varieties the elongation is tangential.

Chemical tests for the presence of Bombay mace are also available (Schneider, J. Pharmacol. 4, 57; Hefelmann, Pharm. Zeit. 1891, 128; Busse, Zeitsch. Nahr. u. Genussm. 1904, 590).

For the estimation of Bombay mace in the presence of Banda mace, provided that Macassar mace be absent, the determination of the fixed ether extract will afford a fair basis for calculation. Soltsien (Zeitsch. offentl. Chem. 3, 253) recommends a preliminary extraction with light petroleum, the extract thus obtained being ten times greater from Bombay than from Banda mace, and Parry (see above table) confirms this.

The information thus obtained should be supplemented by comparison, under the microscope, of the sample with a mixture of Banda and Bombay maces in the proportions indicated. If there is a great discrepancy in the number of the characteristic orange-coloured oil cells the presence of Macassar mace may be suspected. The following test for this variety may also be applied (Griebel, Zeitsch. Nahr. Genussm. 1909, 202):—

Shake up 0·1 gram of the sample with 10 c.c. of light petroleum for 1 minute, filter and mix 2 c.c. of the filtrate with 2 c.c. of glacial acetic acid, and add concentrated sulphuric acid so as to form a layer under the acetic acid solution. In the presence of not less than about 20 p.c. of Macassar mace a red ring forms at the junction of the two layers, within two minutes. Banda mace similarly treated yields only a yellow ring within the same period, whilst Bombay mace produces no colour at all. Comparison experiments with samples of known authenticity should always be made.

Further confirmation of the presence of Bombay mace may be obtained by estimating the essential oil, preferably by Cripps' process (Analyst, 1909, 519), which consists in determining the moisture by heating the spice with calcium carbide, calculating the water from the acetylene involved, and deducting the figure thus obtained from the total loss on heating in a current of air to 135°C., the difference being taken as representing the essential oil. The figures he obtained were as follows:—

	Essential oil
Whole mace	6·1 –10·80 p.c.
Ground mace, unknown origin .	2·86– 7·15 „
Bombay mace . . .	0– 0·67 „

The characters of the fixed oil may also be of use. These are shown in the following table (Spaeth, *ibid.* 1895, 200):—

RESULTS OF EXAMINATION OF THE FIXED OIL OF MACE.

	Melting point	Saponification number	Iodine number	Refraction index	Meissl number
True mace Macassar mace	25·0° to 26·0°	169·9–173·0	75·6–80·8	1·48 -1·487	4·1–4·2 —
Bombay mace	31·0° to 31·5°	189·4–191·4	50·4–53·5	1·463	1·0–1·1

Standards.—The standard fixed by the United States Department of Agriculture is as follows: Mace should contain not less than 20 nor more than 30 p.c. of fixed ether extract; not more than 3 p.c. of total ash; not more than 0·5 p.c. of ash insoluble in hydrochloric acid: and not more than 10 p.c of fibre.

McGill (Bulletin No. 439, Canadian Inland Revenue Department) suggests the following: Ash not to exceed 3 p.c.; ash insoluble in hydrochloric acid not to exceed 0·5 p.c.; crude fibre not to exceed 7 p.c.; ether extract after previous extraction with petroleum ether not to exceed 5 p.c.; ether extract *plus* petroleum ether extract not to exceed 33 p.c. Both the U.S. Dept. of Agriculture and the Canadian Inland Revenue Dept. define true mace as being the Arillus of *Myristica Fragrans.*

Soltsien (Zeitsch. offentl. Chem. 3, 253) suggests that the ether extract after removal of the fat by light petroleum should never exceed 5·5 p.c. C. H. C.

MACE OIL *v.* OILS, ESSENTIAL.

MACKENSITE *v.* THURINGITE.

MACKINTOSHITE. Silicate of thorium, uranium, &c., perhaps $UO_2 \cdot 3ThO_2 \cdot 3SiO_2, 3H_2O$, crystallised in the tetragonal system in forms resembling zircon and thorite. It contains ThO_2 45, UO_2 22, PbO 4 p.c., together with small amounts of lanthanum, yttrium, iron, alkalis, &c. The water is probably due to alteration, and the original mineral probably had the composition $(Th,U)_4Si_3O_{14}$; by further alteration it gives rise to thorogummite. The prismatic crystals and nodular masses are black and opaque with a dull pitchy lustre. Sp.gr. 5·43; H. 5½. The mineral is gelatinised by sulphuric acid, and is readily soluble in a mixture of sulphuric and nitric acids. It is found associated with gadolinite and other rare-earth minerals in pegmatite at Barringer Hill near Bluffton in Llano Co., Texas. L. J. S.

MACLURIN. This substance occurs, together with morin, in the wood of the tropical tree *Chlorophora tinctoria* (Gaudich), which comes into commerce as 'Old Fustic.'

The colouring matters of old fustic were first investigated by Chevreul ('Leçons de chimie appliquée à la teinture,' ii. 150), who described two substances, one sparingly soluble in water, called *morin,* and a second somewhat more readily soluble. Wagner (Jour. f. pr. Chemie, (1), 51, 81) termed the latter *moritannic acid,* and considered that it had the same percentage composition as morin. Hlasiwetz and Pfaundler (Annalen, 127, 351), on the other hand, found that the so-called moritannic acid was not an acid, and as moreover its composition and properties were quite distinct from those of morin, they gave it the name 'Maclurin.'

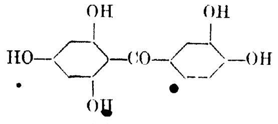
When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the colouring matter. The crude product is crystallised from hot water or dilute acetic acid (Perkin and Cope, Chem. Soc. Trans. 1895, 67, 943). A crude maclurin is also obtained during the preparation of fustic extract, partly in the form of its calcium salt, and this product may be purified with dilute hydrochloric acid and crystallised from water. In order to decolorise the crystals, acetic acid is added to a hot aqueous solution and a little lead acetate in such quantity that no precipitate is formed, and the solution is then treated with sulphuretted hydrogen. The clear liquid thus obtained is much less strongly coloured, and after repeating the operation two or three times, the maclurin, which crystallises out on standing, possesses only a pale yellow tint.

Maclurin, to which the composition $C_{13}H_{10}O_6$ was assigned by Hlasiwetz and Pfaundler (Jahresber. 1864, 558), consists, when pure, of almost colourless needles, which contain one molecule of water of crystallisation; the anhydrous compound melts at 200°C. (Wagner, Jahresber. 1850, 529). The colouring matter is somewhat soluble in boiling water, is soluble in aqueous alkalis, forming pale yellow solutions, whilst with ferric chloride its aqueous solutions give a greenish-black coloration, and with aqueous lead acetate a yellow precipitate, which is soluble in acetic acid. When boiled with potassium hydroxide maclurin yields phloroglucinol and protocatechuic acid.

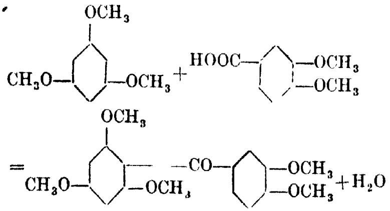
Pentabenzoyl-maclurin $C_{13}H_5O_6(C_7H_5O)_5$, which melts at 155°-156°C., was prepared by König and v. Kostanecki (Ber. 1894, 27, 1996), and *tribrom-maclurin* $C_{13}H_7Br_3O_6{\cdot}H_2O$, colourless needles, by Benedikt.

Maclurin-pentamethyl-ether $C_{13}H_5O(OCH_3)_5$, forms colourless leaflets which melt at 157°C.

König and v. Kostanecki first assigned to maclurin the constitution of a *penta-hydroxy-benzophenone*:

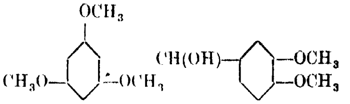


This is supported by the synthesis by W. H. Perkin and Robinson (Chem. Soc. Proc. 1906, 22, 305), and somewhat later by v. Kostanecki and Tambor (Ber. 1906, 39, 4022), of maclurin pentamethyl ether, by the interaction of veratic acid and phloroglucinol trimethyl ether in the presence of aluminium chloride. The reaction may be represented thus:



Maclurin-pentamethyl-ether.

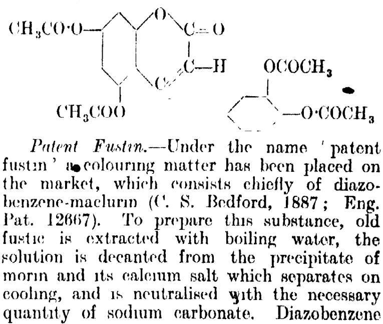
When maclurin pentamethyl ether is digested with alcoholic potash and zinc-dust, *leuco-maclurin-pentamethyl ether* (v. Kostanecki and Lampe, Ber. 1906, 39, 4014) is produced, prismatic needles,



m.p. 109°-110°C., and this on further reduction gives *penta-methoxy-diphenyl-methane*, m.p. 107°-108°C. On the other hand, if leucomaclurin-pentamethyl ether is oxidised in acetic acid solution, *veratric acid* and *dimethoxy-benzoquinone* are formed.

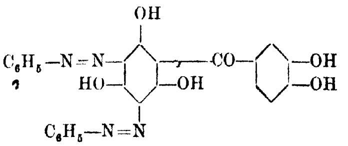
Maclurin itself has been synthesised by Hoesch & Zarzecki (Ber 1917, 50, 462). Protocatechuonitrile is condensed with phloroglucinol in the presence of anhydrous $ZnCl_2$ and a stream of hydrogen chloride. The ketone-imide hydrochloride thus obtained on hydrolysis with boiling water yields maclurin.

By treatment of maclurin with acetic anhydride and sodium acetate, Ciamician and Silber (Ber. 27, 1628, and 28, 1393) obtained a crystalline product which has the composition of a penta-acetyl-maclurin less one molecule of water, viz. $C_{23}H_{18}O_{10}$, and to this compound the following constitutional formula has been ascribed, one of the acetyl groups having undergone condensation with the production of a coumarin derivative, *tetra-acetyl-tetrahydroxy-phenyl-coumarin*:—



Patent Fustin.—Under the name 'patent fustin' a colouring matter has been placed on the market, which consists chiefly of diazobenzene-maclurin (C. S. Bedford, 1887; Eng. Pat. 12667). To prepare this substance, old fustic is extracted with boiling water, the solution is decanted from the precipitate of morin and its calcium salt which separates on cooling, and is neutralised with the necessary quantity of sodium carbonate. Diazobenzene sulphate is then added until a precipitate no longer forms, and this is collected and washed with water. It is sold in the form of a paste, and dyes chrome mordanted wool an orange-brown shade.

Diazobenzene-maclurin (Bedford and Perkin, Chem. Soc. Trans. 1895, 67, 933; *ibid.* 1897, 71, 186), which crystallises in salmon-red prismatic needles, m.p. 270°C. (decomp.), has the following constitution:—



It dyes wool and silk direct from a weakly acid bath, in shades of orange, and on mordants gives colours varying from orange-red on aluminium and orange-brown on chromium, to olive on iron. The dyeings are fairly fast to washing.

With acetic anhydride it yields a *tri-acetyl-derivative* only $C_{13}H_5O_5(C_6H_5N_2)_2\cdot(C_2H_3O)_3$, orange-red needles, m.p. 240° 243°C. (decomp.), which is in keeping with the fact that azobenzol-phloroglucinol yields only a mono-acetyl derivative when treated in like manner.

Dis-azo compounds of maclurin have also been prepared by coupling it with diazotised *o*- or *p*-toluidine, *p*-nitraniline, or sulphanilic acid, and the resulting compounds closely resemble the above described disazobenzene-maclurin.

Dyeing Properties of Maclurin.—With aluminium mordant maclurin gives a pale yellow, with chromium a yellow-green, and with iron a weak grey colour may be obtained.

A. G. P.

MADDER. Madder is the ground root of the *Rubia tinctorium* (Linn.), which has been cultivated for dyeing purposes from a remote antiquity, so remote indeed that one is unable to say with certainty in which countries it originated. It is known to have been employed by the ancient Egyptians, Persians, and Indians, probably by the last in the first instance, and more recently by the ancient Greeks and Romans. About the time of the Crusades the cultivation of madder was introduced into Italy and probably also into France. The Moors cultivated it in Spain, and during the sixteenth century it was brought to Holland. Colbert introduced it into Avignon in 1666, Frantzen into Alsace in 1729, but only towards 1760-1790 did it become important. During the wars of the Republic, its cultivation was largely abandoned, and only after 1815 did this again become regular.

Owing to the beauty and fastness of the tints it yields, and the range in colour that can be produced from it by a variation in the mordant, it was considered until recently as perhaps the most important of all dyestuffs. Although its commercial value has been greatly reduced through the introduction of artificial alizarin, it has still considerable scientific interest.

The plant is an herbaceous perennial belonging to the natural family of the *Rubiaceæ*, and its valuable portion is entirely the root, which is usually of considerable length but does not exceed an ordinary slate pencil in thickness. Old roots are richer in colour than young ones, and the plant is consequently left in the soil for at least 18 and sometimes for 28 months. When removed it is usually washed with water, allowed to dry in the sun or artificially by means of kilns, then finely ground and packed in casks. In certain districts it was stored in pits for several months before grinding, whereby its tinctorial power was said to be greatly enhanced; but these and other refinements of its preparation are now of so little importance as to be hardly worthy of mention. The root in many countries bears the name 'alizari' or 'lizari,' whence we have the name 'alizarin.' Madder was principally cultivated in Holland, France, and Turkey, and to a less extent in Belgium, Italy, and Germany, and North and South America, but the small quantity which enters this country is principally obtained from Holland. Perhaps no substance was submitted to so much examination by the older chemists as madder, and in many of the earlier works on dyeing much space is occupied by a description of these researches.

The isolation of the most important colouring matters of madder, alizarin, and purpurin occurred as far back as 1826 and 1828, and was due to the chemists Robiquet and Colin; but it is doubtful whether they were successful in obtaining these substances in a state of chemical purity. By many of the earlier workers it was considered that these colouring matters did not exist as such in madder, but were present in combination with sugar or some other substance. About 1823 Kuhlmann extracted a bitter-sweet yellow amorphous compound from the root and named it xanthin, and a similar yellow substance was also isolated by Runge and Watt. In 1848 Higgin observed that if a cold aqueous solution of madder, which has a deep yellow colour and an intensely bitter taste, was allowed to stand for some time or was heated to 50°, it lost these characteristics, and a gelatinous flocculent precipitate was formed in which all the tinctorial power of the original infusion resided. Higgin considered, therefore, that the xanthin of madder must, during this process, have been converted into alizarin, and that the change was probably brought about by the action of some ferment contained in the madder, and extracted along with the xanthin by cold water. Somewhat later (1851) Schunck isolated from madder a substance which he called rubian, as a dark brownish-yellow transparent, amorphous hard mass, which by hydrolysis with acids or by the action of the special madder ferment, which he termed 'erythrozym,' was converted into glucose, alizarin, and other substances.

The next important step was due to Rochleder, who prepared the alizarin glucoside in a crystalline condition and named it *ruberythric acid*. It appeared to possess the formula $C_{20}H_{22}O_{11}$, and its hydrolysis could be represented according to the following equation:—

$$\underset{}{C_{20}H_{22}O_{11}}=H_2O+\underset{\text{Alizarin.}}{C_{14}H_8O_4}+\underset{\text{Sugar.}}{C_6H_{12}O_6}$$

Subsequently, Schunck prepared a crystalline compound, rubianic acid, which he regarded as an oxidation product of rubian, and which proved to be identical with the ruberythric acid of Rochleder.

Finally, this portion of the subject was exhaustively examined by Liebermann and Bergami, who assigned the formula $C_{26}H_{28}O_{14}$ to ruberythric acid, and proved that its hydrolysis with acid proceeds as follows:—

$$C_{26}H_{28}O_{14}+2H_2O=C_{14}H_8O_4+2C_6H_{12}O_6$$

For the preparation of the glucoside, madder (1 kilo.) is extracted with boiling absolute alcohol (8–9 litres) for 2 to 4 hours, and the mixture filtered hot. The alcoholic extract is evaporated to about one-quarter its bulk, and on cooling a yellowish-brown crystalline precipitate of the impure glucoside separates. After filtering and evaporating the filtrate still further, crystals of cane sugar separate, and by adding water to the remaining alcoholic solution impure alizarin is precipitated. In this way, according to Liebermann and Bergami, 1 kilo. of madder gave

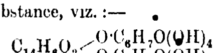
Impure glucoside .	. 50–60	grams	(5–6 p.c.)
,, sugar .	. 15–30	,,	(1·5–3 ,,)
,, colouring matter	30–40	,,	(3–4 ,,)

The impure glucoside, which becomes resinous on drying, is dissolved in water, the solution is precipitated with lead acetate, filtered, and the filtrate treated with basic lead acetate. The pink-coloured precipitate is well washed, suspended in water, decomposed with sulphuretted hydrogen, and the lead sulphide, which contains also the liberated ruberythric acid, is collected and washed with cold water. The ruberythric acid is removed from the lead sulphide by means of boiling alcohol, the yellow extract is partially evaporated, water and some quantity of barium hydroxide solution are added, and, after filtering off a white precipitate, an excess of barium hydroxide is added to the filtrate. The dark cherry-red precipitate of barium ruberythrate is dissolved in acetic acid, the solution is filtered, barely neutralised with ammonia, and then treated with basic lead acetate. The resulting red precipitate is washed with alcohol, suspended in alcohol, and decomposed by hydrogen sulphide, and the liquid and precipitate together are heated to boiling and filtered hot. On cooling, the amber-coloured solution yields pale yellow needles of ruberythric acid which are recrystallised from hot water. The latter portion of this process, employed by Liebermann and Bergami, is due to Rochleder.

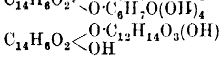
Ruberythric acid crystallises in silky needles of a pure yellow colour, melts at 258°–260°, and when strongly heated yields a sublimate of alizarin. It dissolves in caustic alkali solutions with a cherry-red colour, which on boiling changes to violet, and on acidification yields a precipitate of alizarin. With potassium carbonate solutions, dark red needles of potassium ruberythrate are produced. Ruberythric acid is not precipitated with lead acetate, but basic lead acetate gives a red flocculent precipitate. It possesses no dyeing power.

By the action of sodium acetate and acetic anhydride, Liebermann and Bergami obtained an *octoacetyl* derivative $C_{26}H_{20}O_6(C_2H_3O_2)_8$, which crystallises in yellow needles, melting at 230°.

Schunck and Marchlewski, by means of the method of Schotten and Baumann, obtained a *hexabenzoyl* and a *heptabenzoyl* compound. The fact that ruberythric acid gives an octoacetyl derivative renders two constitutions possible for this substance, viz. :—

(1) 

$$C_{14}H_6O_2 \begin{array}{l} \diagup O{\cdot}C_6H_7O(OH)_4 \\ \diagdown O{\cdot}C_6H_7O(OH)_4 \end{array}$$

(2) 

$$C_{14}H_6O_2 \begin{array}{l} \diagup O{\cdot}C_{12}H_{14}O_3(OH)_7 \\ \diagdown OH \end{array}$$

and of these the second is more probably correct, as an explanation is thus afforded of the well-characterised red-coloured salts which can be obtained from it.

Erythrozym, the madder enzyme, was obtained by Schunck by extracting madder with water at a low temperature (38°) and precipitating the solution with alcohol. When dried, it consisted of a brown amorphous mass. Under its influence, ruberythric acid is hydrolysed with formation of alizarin and glucose. This reaction no doubt takes place in the incompletely dried root on storing, and it is evidently due to this fact that madder was said to dye more readily after this treatment. In dyeing with madder, moreover, the presence of this enzyme will no doubt exercise a beneficial effect, because as it is frequently the practice to employ a cold dye-bath and then to gradually raise the temperature, hydrolysis of the glucoside, which is itself devoid of tinctorial property, will thereby occur with formation of the colouring matter.

Though purpurin is considered to exist in madder in the form of glucoside, such a compound has not yet been isolated, and some uncertainty exists on this point. During some experiments carried out by Perkin, it was found that an alcoholic extract of madder, on standing in cold weather, deposited a considerable quantity of cane sugar contaminated with a red precipitate. This latter was soluble in water, and on treating the solution with cold dilute acid, gave a precipitate of impure purpurin and appeared to consist of an acid calcium salt of this substance. On the other hand, it was not ascertained whether all varieties of madder behave similarly in this respect, and the matter requires further investigation. Presuming, however, that a purpurin glucoside is present in madder, it is evident that this compound is far less stable than ruberythric acid, and is hydrolysed by dilute acids at a temperature at which the latter is unaffected.

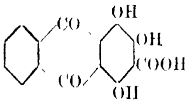
Kopp's Process for the Extraction of Madder.

Based on this assumption, the commercial process of Kopp was devised, and this is specially interesting as it affords a fairly complete method for the isolation of the phenolic constituents of this dyestuff.

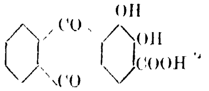
Ground madder is extracted with a cold aqueous solution of sulphurous acid, and the solution, after addition of 2–3 p.c. of hydrochloric acid (33 p.c.), is heated to 60°. A red flocculent precipitate of purpurin is thus thrown down which was collected, washed, dried, and sold under the name of 'commercial purpurine' or 'Kopp's purpurine.' This product was until recently prepared to a very small extent in France for the manufacture of a rose-red lake, and for this purpose gives results differing in some respects from those produced by the artificial dyestuff.

Kopp's purpurine, in fact, is not pure purpurin, but consists mainly of a mixture of this colouring matter with three other substances: *pseudo*-purpurine, purpuroxanthin, and purpuroxanthin carboxylic acid or munjistin.

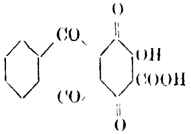
Pseudo-purpurin was first isolated from Kopp's commercial product by Schützenberger and Schiffert, but the fact that it consists of a purpurin carboxylic acid is due to the investigation of Rosenstiehl. It consists of small red prismatic needles, and differs from purpurin in that it is more readily soluble in benzene. It melts at 218°–220° with evolution of carbon dioxide and formation of purpurin, and this decomposition is said to occur gradually at from 180°–195°. Purpurin is also produced by boiling *pseudo*-purpurin with dilute caustic alkali, or by long boiling with water or alcohol. The constitution of *pseudo*-purpurin is represented by the following formula :—



It may be prepared synthetically (D. R. P. 260765) by dissolving 1 : 2-dihydroxyanthraquinone-3-carboxylic acid—

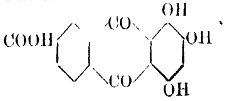


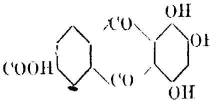
in 20 parts of sulphuric acid and slowly treating the solution at 15°–20° with 0·3–0·4 parts of manganese dioxide. In place of the 1 : 2-dihydroxy the 1 : 4 : 3-dihydroxycarboxylic acid may be employed (D. R. P. 272301), in which case the 2-hydroxyanthradiquinone carboxylic acid is the first product of the reaction—



This by means of sodium hydrogen sulphite solution is reduced to *pseudo*-purpurin

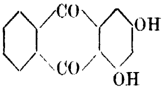
It is interesting to observe that an isomeric compound which is obtained by the oxidation of alizarin carboxylic acid, and for which also the two formulæ—





are possible, differs markedly from *pseudo*-purpurin, and is an exceedingly stable compound (Perkin and Cope)

Purpuroxanthin or xanthopurpurin, which forms glistening yellow needles, melting at 262°–263°, is a dihydroxyanthraquinone isomeric with alizarin, and was isolated from Kopp's purpurine by Schützenberger and Schiffert. These authors also found that purpuroxanthin can be produced by digesting purpurin with phosphorus iodide and water, or by the action on it of a boiling alkaline stannous chloride solution. The reverse action occurs, according to Rosenstiehl, when an alkaline solution of purpuroxanthin is boiled with excess of air, purpurin being thus produced. Purpuroxanthin was synthesised by Noah by heating 3 : 5-dihydroxybenzoic acid with benzoic acid in the presence of sulphuric acid, and possesses the following constitution :—



According to Plath, the dimethyl ether melts at 178°–180°, and the diacetyl derivative (Liebermann) at 183°–184°.

Purpuroxanthin dyes aluminium mordanted fabrics a yellow colour (Schützenberger and Schiffert).

Purpuroxanthin carboxylic acid (munjistin) was discovered by Schunck and Römer in the crude purpurin. It crystallises from acetic acid in golden yellow leaflets, melts at 231°, and dissolves in alkaline solutions and ammonia with a red coloration. By heating above its melting-point or by boiling with alkalis, it is converted into purpuroxanthin. It has not been prepared synthetically, but probably contains its carboxyl group in a similar position to that present in *pseudo*-purpurin. It is said to dye aluminium mordanted fabrics an orange-red colour, which is, however, not fast to the action either of soap or light.

Green alizarin. The sulphurous acid liquid from which the purpurin precipitate has been removed is boiled for 2 hours, when the ruberythric acid and certain other glucosides present are hydrolysed and a deep green precipitate separates. This at one time was a commercial article, and was known under the name of 'green alizarin.'

Chlororubin.—The green tinge of this product arises from the presence in madder of a considerable quantity of a peculiar substance, possibly a glucoside, termed chlorogenin or rubichloric acid, but little or nothing is known of its chemical nature. It is also present in chay root, morinda root, in certain species of *galium* and in the *Gardenia grandiflora.* This compound, which has been obtained in the form of a colourless syrup and to which the formula $C_{14}H_8O_9$ has been assigned, on digestion with boiling dilute mineral acid, is converted into chlororubin and formic acid. Chlororubin consists of a dark green amorphous powder which is insoluble in all the usual solvents, but dissolves in alkaline solutions with a blood-red colour.

Yellow alizarin.—In order to obtain this product, the dried and finely powdered 'green alizarin' was extracted at 150° with petroleum (toluene or coal-tar solvent naphtha is more suitable for laboratory purposes), by which means the alizarin and other phenolic constituents pass into solution, whereas the chlororubin remains undissolved. The petroleum extract after cooling is agitated with 10 p.c. caustic soda solution, and the dark violet-coloured alkaline liquid thus produced is removed and neutralised with acid. The bright yellow precipitate was collected, washed and dried, and sold under the name of 'yellow alizarin.'

The alizarin prepared in this manner is not completely pure, as it contains a small quantity of a mixture of non-tinctorial substances, which are derivatives of anthraquinone. To remove these, an alkaline solution of the 'yellow alizarin' is treated with milk of lime, which precipitates the alizarin in the form of its calcium compound. This when collected, well washed, and decomposed with acid, gives a very pure alizarin which is best crystallised from solvent naphtha.

If the reddish-brown filtrate from the calcium alizarate is neutralised with acid, a small quantity of a dull yellow precipitate separates which is approximately equal to 0·02 p.c. of the madder employed. A preliminary examination of this product indicated that it consisted of at least four yellow crystalline substances, with no special properties that would permit of their ready separation.

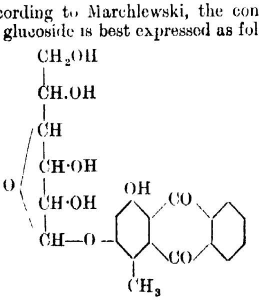
Schunck during his examination of madder obtained various yellow crystalline and amorphous products by the action of acids and alkalis on his rubian. The individuality of most of these substances, to which the names rubiretin, verantin, rubiadin, rubianin, rubiafin, rubiagin, rubiadipin, rubidehydran, rubihydran, and rubiacic acid were assigned, has been doubted by later writers, and but one of these—namely, rubiadin—has been characterised. On the other hand, it is quite possible that certain of these may exist in the mixture of yellow non-tinctorial substances previously referred to. For a description of his compounds, the original papers of Schunck should be referred to.

Rubiadin glucoside (Schunck and Marchlewski).—Madder is extracted with boiling water, the solution precipitated with lead acetate, and the filtrate treated with ammonia, by which means a second lead precipitate is formed. The latter is decomposed with sulphuric acid, the lead sulphate removed, and the clear liquid boiled with addition of hydrochloric acid. A dark green precipitate separates, only a portion of which dissolves in boiling alcohol. On treating the alcoholic extract with lead acetate, the alizarin present can be removed, and addition of baryta water now precipitates the barium salt of the rubiadin glucoside, which is decomposed by dilute hydrochloric acid. It crystallises from alcohol in citron-yellow needles, melts at 270° with decomposition, and when hydrolysed by acid gives rubiadin and glucose—

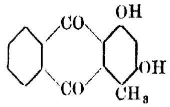
$$C_{21}H_{20}O_9+H_2O=C_{15}H_{10}O_4+C_6H_{12}O_6$$

Penta-acetylrubiadin glucoside, yellow needles, melts at 237°.

According to Marchlewski, the constitution of this glucoside is best expressed as follows:—



Rubiadin, prepared by the hydrolysis of the glucoside, forms yellow needles, melting about 290°, soluble in alkalis with a red coloration. By oxidation with chromic acid it gives phthalic acid. Rubiadin, according to Schunck and Marchlewski, is a methyl purpuroxanthin and possesses the following constitution:—



Rubiacin (Runge's madder orange) is a yellow crystalline substance obtained directly from the madder root, and is formed, according to Schunck, by the decomposition of a glucoside. It separates in small quantity from an infusion of madder made with only a little cold water, after it has become sour by 12 hours' standing. It crystallises in the form of plates and needles, having a strong reddish-green lustre. Alkalis dissolve it with a purple colour.

The following table illustrates the analysis of madder by the sulphurous acid extraction method:—

Madder is extracted with dilute sulphurous acid solution and the extract heated to 60°.

Precipitate consists of
Purpurin,
Pseudo-purpurin,
Purpuroxanthin carboxylic acid,
Purpuroxanthin.

Filtrate is digested with boiling dilute H_2SO_4, and the resulting precipitate of green alizarin extracted with boiling toluene or petroleum.

Chlororubin remains undissolved.

The toluene extract is agitated with caustic soda solution, and the alkaline liquid is treated with baryta water.

Precipitate consists of calcium alizarate, which when decomposed with acid gives alizarin.

Filtrate on acidification gives a precipitate of yellow non-tinctorial derivatives of anthraquinone

COMMERCIAL PREPARATIONS OF MADDER.

The principal of these were: Garancine, Garanceux, Flowers of Madder, Commercial Alizarin or Pincoffin, and Madder extract.

Garancine.—The preparation of this product results from the observation in 1827 of Robiquet and Colin, that by treating ground madder with an equal weight of concentrated sulphuric acid, the various principles of the madder were destroyed with the exception of the colouring matter alizarin. We now know further that the glucoside of the root is decomposed by the action of the acid. This first product was termed *charbon sulphurique*, but soon the method of its preparation was slightly altered, and it then received the name *garancine*.

Garancine is made by mixing, in a wooden tank with false bottom, 100 kilos. ground madder, 1000 litres water, and 2 kilos. sulphuric acid, 168°Tw. (sp.gr. 1·84), stirring up and allowing the whole to macerate for about 12 hours. The liquid is then drawn off, the residue mixed with a little water and 30 kilos. strong sulphuric acid, and the whole boiled for 2–3 hours. After running off the acid liquor, the garancine remaining is washed with water till free from acid, drained, pressed, dried, and ground.

The colouring power of garancine is three to four times that of good madder, it dyes more readily, giving yellower-toned reds and pinks, and greyer lilacs. They are not quite so fast to soap as the madder colours, but since, in the case of printed calicoes, the unmordanted white parts are not so much soiled in the dye-bath, the operation of soaping can be omitted.

Garanceux or *Spent Garancine* was introduced in 1843 by L. Schwarz of Mulhouse. It was simply a low quality of garancine prepared in the above manner from the spent madder of the dye-baths, and made by each calico-printer for himself, by way of economy. Its colouring power is about one-fourth that of good garancine.

Flowers of Madder was first made in 1851 by Julian and Rogner of Sorgues. It can be prepared by macerating ground madder for several hours with cold water very slightly acidulated with sulphuric acid (1–2 p.c. on the weight of madder), then washing, draining, pressing, drying, and grinding. In this manner all soluble, mucilaginous, and sugary matter, &c., is removed, decomposition of the glucoside by fermentation occurs, and the residue has nearly double the colouring power of the original madder. The waste liquors were neutralised, allowed to ferment with the addition of yeast, and then distilled to gain the alcohol. 100 kilos. madder yielded 45 60 kilos. flowers of madder and 10 litres alcohol, suitable for making varnish, &c.

Commercial Alizarin or *Pincoffin* was introduced in 1852 by Schunck and Pincoff, who prepared it by submitting ordinary garancine to the action of high pressure and superheated (150°C.) steam. By this treatment the verantin and rubiretin present in the garancine were said to be destroyed, while the alizarin remained intact, and the product yielded in consequence more brilliant purples, and less soaping was required to clear the whites or unmordanted portions of printed calicoes.

Madder Extracts.—Already in 1826 attempts were made by Gaudin to apply mordants along with the colouring matter of madder directly to calico, in the form of an extract, *i.e.* as a steam-colour, instead of by dyeing, and in 1837 Gastard succeeded in doing this successfully on a large scale by means of a product named *colorine*. The expense, however, of this and other early madder extracts retarded their application, but their utility having been clearly demonstrated, the endeavours of numerous chemists were directed to their production in a reasonably cheap manner. Madder extracts consisted of variable mixtures of the two colouring matters of madder, alizarin and purpurin, or of each separately, in a more or less pure condition. By the introduction of artificial alizarin, just when their manufacture had been perfected, they lost all their importance. The following were the chief methods of production employed.

Schutzenberger's process consisted in first extracting all the purpurin from ground madder by water heated to 55°C., and afterwards dissolving out the less soluble alizarin from the dried residual madder by means of wood-spirit. The aqueous solution was precipitated by lime, the washed calcium-purpurin lake was then decomposed with hydrochloric acid, the liberated purpurin collected and washed, when it was ready for use. The alcoholic solution of alizarin was merely precipitated by water, collected and washed. Alizarin and purpurin extracts were thus obtained.

Paraf's method (1868) consisted in extracting madder with superheated water, with or without the addition of a small quantity of alum or sulphuric acid, then collecting and washing the flocculent alizarin precipitate which separated out on cooling.

The modes of preparing Kopp's 'purpurine,' 'green alizarine,' and 'yellow alizarine' have already been given.

Pernod's madder-extract, once largely used, was prepared by extracting garancine with boiling water very slightly acidified with sulphuric acid, collecting and washing the precipitate thrown down on cooling, and extracting the dried precipitate with boiling alcohol. After recovering the major portion of the alcohol by distillation, the remaining solution was mixed with water, and the precipitated alizarin was collected and washed.

USE OF MADDER IN DYEING.

Previous to 1870 madder and its derivative garancine were the dyestuffs *par excellence* of the calico-printer and Turkey-red dyer.

By the former, it was used because of its characteristic property of yielding a variety of colours with the aluminium, tin, and iron mordants, viz. red and pink, orange, lilac, and black; also brown or chocolate, by employing a mixture of aluminium and iron mordants. Further, all these colours are fast to soap and light. To the calico-printer both the alizarin and the purpurin of the madder were of use, though undoubtedly the alizarin would, in most styles of work, be the essential colouring matter. The Turkey-red dyer employed madder, and afterwards garancine, because they yielded, by his peculiar process, the most brilliant and most permanent red on cotton which was known. In this case the alizarin was the all-important colouring matter, since the purpurin, although fixed on the fibre at first, was more or less removed during the operations of clearing. Alizarin, in conjunction with aluminium and iron mordants, gives a bluish-red and a comparatively bright lilac; purpurin, a yellowish-red and a greyish-lilac, respectively.

The method of applying madder in Turkey-red dyeing was similar to that now employed in the case of alizarin.

Another interesting feature in connection with the application of this dyestuff is that, if the madder was deficient in lime, it was necessary to add a certain proportion of chalk to the dye-bath; it now appears that calcium is a normal constituent of the madder colours, especially those obtained with aluminium and iron mordants.

Madder has also been used in the past, and is even now employed to a small extent, by the indigo dyer and the woollen dyer.

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MADDER CAMPHOR *v.* CAMPHORS.

MADDER LAKE *v.* LAKES.

MAFOUREIRA NUT. A nut imported from Portuguese East Africa containing about 60 p.c. of fat, solid at ordinary temperatures and consisting mainly of palmitin and olein, together with some free fatty acids, chiefly oleic acid. Used in the manufacture of lubricants, soap, and candles. The supply is practically unlimited, the tree bearing the nut growing wild all over the country.

MAGDALA RED *v.* AZINES.

MAGENTA *v.* TRIPHENYLMETHANE COLOURING MATTERS.

MAGISTERY. The term magistery was employed by the older chemists to denote the white precipitates which form on the addition of water to strongly acidified solutions of certain metals.

MAGISTRAL. An old medical term signifying a sovereign remedy, employed by the Spanish smelters of Mexico and South America to the roasted and powdered copper pyrites, which is added to the stamped silver ores in the *torta* or magma, obtained in the *patio* process of decomposing horn silver (*v.* SILVER).

MAGMA. A pasty or semifluid mixture. Applied in medicine to the residuum obtained after expressing certain substances to extract the fluid parts of them, or after treating a substance with some menstruum; a thick ointment or confection (Dunglison). *See also* LAVA.

MAGNALIUM. An alloy of magnesium and aluminium (*v.* ALUMINIUM).

MAGNESIA ALBA. A hydrated basic magnesium carbonate (*v.* MAGNESIUM).

MAGNESIA NIGRA. An old name for native manganese dioxide (*v.* MANGANESE).

MAGNESITE (Fr. *Giobertite*). A mineral consisting of magnesium carbonate $MgCO_3$, and belonging to the calcite group of the rhombohedral carbonates. To French mineralogists it is known as giobertite or baudissérite, the name magnésite being applied by them to meerschaum. Crystals are of rare occurrence: they usually have the form of the primary rhombohedron, parallel to the faces of which are perfect cleavages. The angle between the faces of this rhombohedron is 72° 36′ (the corresponding angle in calcite being 74° 55′). Sp.gr. of crystals, 3·02; hardness, 4. Of the massive material there are two distinct varieties—crystalline and compact. The former consists of a spathose aggregate, showing bright cleavage surfaces, of varying degrees of coarseness, and sometimes so fine as to resemble a saccharoidal marble. The compact or cryptocrystalline variety, sometimes described as amorphous, is snow-white and has much the appearance of chalk or unglazed porcelain; this has sp.gr. 2·9 to 3·0. Analyses of massive material show 85 to 96 p.c. $MgCO_3$, with calcium and iron carbonates and often (especially in the compact variety) a little silica. A ferriferous variety of the spathose form, known as breunnerite or brown-spar, contains 5 to 30 p.c. $FeCO_3$ isomorphously replacing magnesium carbonate and forms a passage through mesitite (*q.v.*) to chalybite; here the sp.gr. ranges up to 3·2.

	I.	II.	III.	IV.	V.	VI.
MgO	44·53	46·77	46·61	46·23	46·59	42·43
CaO	2·79	0·44	0·40	0·31	0·32	1·68
FeO		—	—	1·01	0·64	3·53
Fe_2O_3	0·26	0·40	0·21	—	—	—
Al_2O_3	0·34	0·10	0·14	—	0·19	0·03
SiO_2	2·10	0·31	0·73	0·46	0·66	0·92
CO_2	49·94	51·44	51·52	50·32	51·79	50·41
	99·96	100·06	99·61	98·33	99·90	99·53

I. Compact magnesite from Eubœa (A. Christomanos, 1903).

II. Compact magnesite from Chalk Hills, Salem (H. H. Dains, 1909, also H_2O 0·60).

III. Compact magnesite from Alameda claim, Santa Clara Co., California (F. L. Hess, 1908)

IV. Crystalline, marble-like magnesite from Valley, Stevens Co, Washington (U.S. Geol. Survey, 1918).

V. Crystalline magnesite from St. Kathrein, Styria (C. v. John, 1907)

VI. Crystalline breunnerite from Veitsch. Styria (R. Banco, quoted by K. A. Redlich, 1914; also MnO 0·53).

The compact variety of magnesite occurs as an alteration product of serpentine rocks, in which it forms veins, interlacing networks, and large irregular masses Deposits of this kind are worked commercially on the island of Eubœa in the Grecian Archipelago, the 'Chalk Hills' near Salem in Madras, at several places in California, Transvaal, and in Piedmont; and several other localities are known. The spathose variety of the mineral occurs as beds and lenticular masses in metamorphosed sedimentary rocks, in association with limestone, dolomite, and spathic iron ores; and has probably originated by the action of solutions of magnesium salts on limestone. Deposits of this type are worked at Grenville in Quebec, Stevens Co. in Washington, and in Austria. The Austrian deposits extend from the Tyrol into northern Hungary with a maximum development in Styria Here the predominating mineral is the breunnerite variety.

Magnesite is used for the preparation of Epsom-salts and other salts of magnesium, and for the production of carbon dioxide. Calcined magnesite is made into refractory bricks for lining basic steel furnaces and electric furnaces. For this purpose the ferriferous breunnerite variety has the advantage that it sinters somewhat when calcined. The strong cement (oxychloride or Sorel cement) made by mixing partially calcined magnesite with magnesium chloride solution is employed for the construction of fireproof partitions, flooring, artificial stone, tiles, emery-wheels, grindstones, lithographic stone, &c. For this purpose the compact variety is best suited. Other applications of magnesite are in the manufacture of paper and paint, and as a non-conducting covering on boilers and steam-pipes.

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L. J. S.

MAGNESIUM. Sym Mg. At.wt. 24·375 Magnesium appears to consist of three isotopes of masses 24, 25, and 26, which occur in the proportion 6 : 1 : 1 and give an average atomic weight of 24·375. The compounds of magnesium most widely occurring in nature are *magnesite* $MgCO_3$, *kieserite* $MgSO_4,H_2O$, *kainite*

$$MgSO_4{\cdot}KCl,6H_2O$$

carnallite $MgCl_2{\cdot}KCl,6H_2O$, and the many silicates, as *enstatite, talc, meerschaum, augite, olivine*, and *serpentine*. Together with calcium it frequently occurs in huge mountain masses as *dolomite* $(MgCa)CO_3$. The sulphate $MgSO_4,7H_2O$ is one of the principal saline constituents of many springs, and the chloride occurs in sea water.

Preparation of the metal.—Magnesium, in an impure state, was first obtained by Davy in 1808 by electrolysis, and also by reducing the oxide in a current of the vapour of potassium. In 1830, Bussy obtained it in larger quantity and in a purer form by heating anhydrous magnesium chloride to redness with potassium. On dissolving out the residual chlorides the metal was obtained as a powder which could be readily fused into globules. Bunsen subsequently prepared it by electrolysis of the fused chloride, using a battery of ten zinc-carbon cells. The operation was conducted in a porcelain crucible, of which the upper part was divided by a vertical partition, ground to the right size out of an ordinary crucible lid. The crucible was fitted with a tile cover, through which the poles of gas carbon were inserted, one on each side of the partition. The negative carbon pole was cut like a saw, in such a manner as to form overhanging ledges, under which the light magnesium collected, and was thus prevented from floating to the surface and burning at the high temperature employed.

As the anhydrous chloride is difficult to prepare, Matthiessen improved the process by substituting a mixture of three equivalents of potassium chloride with four of magnesium chloride. A little ammonium chloride is added, the mixture fused and electrolysed in Bunsen's apparatus; it is, however, unnecessary to cut the negative pole, as the magnesium is heavier than the fused mixture. In small quantities, the metal may be readily obtained by electrolysing this mixture in a clay tobacco pipe heated over a lamp, the negative pole being formed by an iron wire inserted down the stem, and the positive by a piece of gas-carbon just touching the surface of the fused mass.

Manufacture.—The first steps towards the preparation of magnesium on an industrial scale were taken by Deville and Caron, whose process essentially consisted in heating a mixture of anhydrous magnesium chloride, fluorspar, and sodium. In the earlier experiments 600 grams of the fused chloride, 480 grams of finely-powdered fluorspar, and 230 grams of sodium in small pieces were employed. The fused magnesium chloride is obtained by evaporating to dryness a mixed solution of magnesium and ammonium chlorides, and fusion of the residue. Magnesium chloride alone cannot be fused without decomposition, hence the use of the ammonium chloride, which prevents this.

The dry mixture, in the proportions mentioned, is then introduced into a red-hot earthen crucible and the cover pressed down by a weight while the violent reaction occurs. When all action ceases, the contents are stirred with an iron rod, which causes the minute globules of metal to coalesce. After being left to cool, all the magnesium may be collected as a ball upon the rod before the melt becomes solid. The metal is then hammered to free it from slag, and should amount to about three-fourths of the theoretical equivalent of the sodium used.

Wöhler subsequently showed that the troublesome preparation of the anhydrous chloride may be avoided by using instead a mixture of magnesium chloride with one-sixth of its weight of sodium chloride, or of a mixture of sodium and potassium chlorides.

Deville and Caron also showed that the metal may be distilled at nearly the same temperature as zinc, in carbon-lined vessels, in an atmosphere of hydrogen, and were thus enabled to obtain it in a very pure form, free from carbon, silicon, and nitrogen.

Sonstadt, in 1863, introduced a few improvements in the process of Deville and Caron. An iron crucible was substituted for the earthen one, and the mixture used consisted of magnesium and sodium chlorides with one-fifth its weight of sodium. The heating was continued for about half an hour after the whole crucible has been raised to full redness.

In a later patent, Sonstadt extended the whole process to a manufacturing scale, and adopted an enlargement of Deville and Caron's method of purification by distillation. The 'magnesium still' consisted of two wrought-iron vessels placed vertically over each other; the upper one served as the crucible, and was connected with the lower one, which acted as receiver, by means of an iron condensing tube, which projected upwards into the crucible to within an inch of the lid. The whole apparatus could be rendered air-tight. The crucible filled with crude magnesium to the level of the top of the tube was fixed in a furnace and surrounded by fuel; the receiver was fitted into a recess of the fire grating, and projected below. Before commencing the distillation, the wrought-iron lid was screwed down, and the air displaced by a current of hydrogen or coal-gas. The receiver was cooled by external application of water. The crucible was maintained at an almost white heat until the operation was complete. The whole apparatus was then removed from the furnace and cooled; on taking to pieces, the magnesium was found as a solid mass in the receiver. This was then remelted and cast into ingots.

Magnesium was formerly prepared on a large scale in this country by the Magnesium Metal Company, at Patricroft, near Manchester.

Von Püttner (Eng. Pat. 1031, Jan 24, 1885) prepared the metal by a process very like the reduction of zinc, which metal magnesium very closely resembles. The magnesium mineral is first treated so that the metal is present entirely as oxide. This is then intimately mixed with carbonaceous matter, to which may advantageously be added oxide of iron, and heated to whiteness in retorts. The vaporised metal is condensed and collected in receivers similar to those used in the zinc manufacture.

Matignon (C. R. 1913, 1157) obtained metallic magnesium by heating heavy magnesium oxide with aluminium powder in an exhausted steel tube at 1200°C. The reaction is almost complete, the magnesium being deposited in a crystalline state in the cooler part of the tube.

Gerhard and Smith (Eng. Pat. 16651, Dec. 19, 1884) describe a process for the electrolytic deposition of magnesium as follows. Magnesium ammonium sulphate is prepared by crystallising together 228 parts of magnesium sulphate and 132 parts of ammonium sulphate. This is dissolved in 35,000 parts of water, and the electrodeposition is effected in this solution at a temperature from 150° to 212°F. If a white metal is desired, a nickel anode is employed; for magnesium bronze, a copper anode. In the latter case the most suitable bath is formed by dissolving 360 parts of magnesium ammonium sulphate, 550 parts of potassium cyanide, and 550 parts of ammonium carbonate in 35,000 parts of water.

The electrolytic method has now superseded the chemical method. Briefly the details of the process, according to Borchers, are as follows. An anhydrous electrolyte consisting of chlorides having the composition corresponding to the formula $MgCl_2 \cdot KCl \cdot NaCl$ is prepared by heating the crystallised salts in an iron pan. Magnesium chloride cannot be used alone, as it decomposes on heating with the liberation of hydrochloric acid and the formation of oxychloride. This reaction takes place to a certain extent in spite of the presence of the alkaline chlorides; and if the oxide is not removed, as also any magnesium sulphate present, the globules of magnesium formed during electrolysis fail to unite to form a clean metal. The sulphate is therefore decomposed after fusion of the chlorides by stirring in some carbon or sawdust, when oxide is produced. The oxide is then converted to chloride by the addition of ammonium chloride, when a clear bath should result. The fused mass is then emptied into the electrolytic cells, which are usually of iron and form the cathode. The anode is a carbon rod surrounded by a porcelain cylinder and cap from which a tube passes for leading off the chlorine. The apparatus is kept in a furnace and the temperature is maintained somewhat above the melting-point of magnesium. The current density is about 1000 ampères per square metre with a pressure of 7 to 8 volts. The resulting metal and salts are poured into a mould, and after cooling the buttons of magnesium are separated and remelted with pure carnallite in an iron crucible, the temperature being raised until the magnesium floats on the flux, and is so liquated from impurities. The magnesium is ladled off, remelted, and poured into ingots.

According to U.S. Pat. 1258261 (Chem. and Met. Eng. 1919, 87) the chlorides of magnesium and potassium in a molten condition are electrolysed, using a carbon anode and a cathode of molten tin or copper. The magnesium separated from the electrolyte is alloyed with the molten cathode, which is removed when it contains sufficient magnesium for further treatment. In the second step the magnesium alloy is used as anode, the electrolyte is the same nature as before except with the addition of a heavy salt of an electro-positive metal such as barium chloride. In the second electrolysis magnesium enters into the solution from the impure anode and deposits in the cathode so arranged that the magnesium separated may float upon the electrolyte. In 1918 America produced 284,188 lbs. of magnesium valued at $615,217, about three fifths of the total being sold as sticks and two-fifths as powder. Its purity varied from 99 to 99·9 p.c.

The Dow Chemical Co. uses magnesium chloride for the manufacture of the metal. This chloride is a by-product from its salt and bromine industry in the Saginaw Valley, Mich. The hydrated magnesium chloride, mixed with common salt in the proportion of 4 to 1, and with a small quantity of ammonium chloride, is heated in shallow vats over a slow coal fire to remove its combined water. About 50 p.c. of the water is driven off in this way. The partly dehydrated mixture is removed from the vats, cooled, and then completely dehydrated in a second furnace at a higher temperature. The metal is then produced by electrolysis of the fused magnesium chloride in a bath of sodium chloride and ammonium chloride. The electrodes used are graphitised carbon, and electrolysis takes place in cylindrical sheet-iron cells, which serve as cathodes.

The American Magnesium Corporation uses magnesite mined on the Pacific Coast, and calcined before shipment to the plant at Niagara Falls, N.Y. The electrolyte or bath is a mixture of fused fluorides, the oxide going into solution and being decomposed by the electric current. The slag is removed and the metal drawn from the furnaces at hourly periods and poured into small ingot moulds. The metal is refined by remelting the ingots in small retorts. Most of the magnesium now used is employed in foundries as a deoxidiser or scavenger in brass, bronze, copper, nickel, and aluminium. It was for a time used chiefly in the production of flares, tracer bullets, and special explosives, and as a flashlight in photography; it is also used in a small way in making alloys with other metals (R. W. Stone, U.S Geol. Survey Report, through Chem. Trade Journ. October 8, 1921, 434).

Properties.—Magnesium is a brilliant white metal resembling silver. When heated *in vacuô* to the temperature of the softening of porcelain it sublimes, and deposits itself upon the cooler parts of the vessel in beautiful silver-white crystals (Dumas, Compt. rend. 90, 1027). During the heating it gives off about one and a half times its volume of gas; 20 grams of the metal yielded 12·3 c.c. of hydrogen and 4·1 c.c. of carbon monoxide. The faces of the crystals are often curved and the edges rounded; the usual form is a regular hexagonal prism, the basal planes being less brilliant than the prism faces. The angle of the corresponding rhombohedron is 80° 3′, and is intermediate between those of zinc and arsenic (Des Cloizeaux, Compt. rend. 90, 1101). Its sp.gr. is 1·74–1·75. It melts at 651°, and the boiling-point is a little higher than that of zinc. It preserves its silvery lustre in dry air, but soon tarnishes in moist air owing to the formation of a film of hydrated oxide. It is readily malleable, but only ductile at high temperatures. Average coefficient of expansion between 0° and 100°, 0·0000259. On the large scale it is usually pressed into wire while in a state of semi-fluidity, and is then frequently flattened into ribbon. It burns when heated in a flame in air with an intense white light, very rich in the chemically active violet rays; hence its use in photography. According to Roscoe, a burning magnesium wire of 0·297 mm thickness evolves as much light as 74 stearin candles of which five go to the pound. The light of burning magnesium is also employed in signalling and pyrotechny. For the production of the so-called 'Bengal lights,' the following mixtures are recommended. For white fire, 1 part shellac is fused with 6 parts barium nitrate, the fused mixture ground and mixed with 2·5 p.c. of powdered magnesium. For red fire, 1 part shellac is fused with 5 parts strontium nitrate, and the ground mass mixed with 2·5 p.c. of magnesium. These mixtures may either be made into ribbons about a finger's breadth or may be charged into thin zinc tubes so as to serve as torches. On burning, the zinc case burns along with the mixture. Star shells are made of a mixture of magnesium powder with barium nitrate and potassium nitrate, or the magnesium powder may first be mixed with a certain proportion of aluminium powder.

The strength of magnesium has been determined at the mechanical experimental station at Charlottenburg, and shown to be very considerable. Its breaking coefficient for tensile strain per square mm. is 23·2 kilos.; specific resistance to compression, 27·2 kilos. per square mm.; bending strength, 17·4 kilos. At a temperature of 450° it can be rolled, pressed, worked, and brought into complicated forms. Screws and threads of magnesium are considerably sharper and more exact than those of aluminium (J. Soc. Chem. Ind. 6, 730). It is quite as resistant to corrosion as aluminium, whilst it is superior to it in heat conductivity, and equal to it in electrical conductivity. The metal is barely attacked by a mixture of strong sulphuric and fuming nitric acids.

Magnesium has no action on pure water, but in presence of a trace of platinum chloride it decomposes water rather quickly, evolving hydrogen and forming magnesium hydroxide. Powdered magnesium reacts with water of crystallisation, being most active with halogen salts. $SnCl_2,2H_2O$ and $Fe_2Cl_6,6H_2O$ show the greatest activity. Hydroxides of lead, calcium, and aluminium which contain no water of crystallisation do not react even at 200°. Platinised magnesium constitutes a good deoxidising agent; it reduces nitrobenzene, for instance, completely to aniline (Ballo, Ber. 16, 694). Dilute acids rapidly dissolve it with violent evolution of hydrogen; with dilute hydrochloric acid it inflames when first thrown in. Strong sulphuric acid acts slowly, and a mixture of this acid with fuming nitric acid has no action upon it at ordinary temperatures. Solutions of caustic alkalis have no action upon it, but, heated with solutions of ammonium salts, it evolves hydrogen and dissolves, forming a double salt of ammonium and magnesium. Aqueous solutions, however, of acid sodium or potassium carbonates, as well as solutions of carbonic acid, dissolve the metal with evolution of hydrogen (Ballo, Ber. 15, 3003). Magnesium burns when heated in chlorine gas or bromine vapour, and especially brilliantly in the vapours of sulphur and iodine. It combines at determinate temperatures, when in a finely divided state, with sulphur, phosphorus, and arsenic, and at a red heat decomposes oxides of carbon, sulphur dioxide, and many hydrocarbons. Silica and boric acid are readily reduced by it. It combines directly with nitrogen, forming a crystalline nitride Mg_3N_2. It precipitates nearly all the metals from their neutral solutions in the metallic state; aluminium, uranium, and chromium as oxides.

Magnesium may be advantageously employed in place of zinc in toxicological investigations, owing to its freedom from arsenic. It may likewise be used instead of zinc in voltaic batteries, owing to its higher electromotive force (Roussin, J. Pharm. Chim. [iv.] 3, 413).

Alloys.—Magnesium forms malleable alloys with potassium and sodium, which decompose water at ordinary temperatures. 15 parts of magnesium form with 85 parts of tin a brittle lavender-coloured alloy, which also decomposes water. An alloy with 5 p.c. of thallium is stable and more malleable than pure magnesium. With mercury, it does not appear to form an amalgam at ordinary temperatures. Alloys with aluminium, zinc, cadmium, lead, bismuth, antimony, silver, gold, and platinum have also been prepared (Parkinson, Chem. Soc. Trans 1867, 125) by fusing the metals together in a current of hydrogen, or by fusion in an earthen crucible under a flux of equal parts fluorspar and cryolite, or one part fluorspar with two parts of common salt. The magnesium is attached to the end of an iron rod and well stirred among the other metal, otherwise, being so light, it would float to the top. Triple alloys are also obtained with bismuth and copper, copper and gold, and with copper and nickel. Most of these alloys are brittle, and of little use in the arts.

Magnesium and zinc form a single compound $MgZn_2$ and no solid solution (Compt. rend. 1910, 904). Broniewski, from his investigations of alloys of aluminium and magnesium, comes to the conclusion that two definite compounds, AlMg and Al_2Mg_3, exist. These form a continuous series of solid solutions. 'Duralumin' is aluminium alloyed with a small percentage of magnesium and copper. It has the property of hardening, like steel, on heating and quenching. Magnesium alloyed with small amounts of zinc gives a strong alloy which can be wrought and rolled, and presents the fracture of fine steel. It resists the action of air and water and can be cast and turned like brass and copper. 'Electron' contains 95 p.c Mg, 4·5 p.c. Zn, and 0·5 p.c Cu. Sp.gr. 1·78. The mechanical properties of the alloy are: Yield point 12·0, maximum load 16·1–18·1, crushing load 23·0 tons per sq. in., elongation 13–19 p.c.

Alloys of magnesium and lead containing from 5 to 50 p.c. of magnesium and 95 to 50 p.c. of lead when exposed to moist air rapidly absorb oxygen, and crumble to a black powder consisting of magnesium hydroxide $Mg(OH)_2$ and hydrated lead suboxide, $Pb_2(OH)_2$. It has been suggested that these alloys might be used for removing oxygen in gaseous mixtures as in the case of hydrogen for aircraft purposes (Ashcroft, Trans. Faraday Soc. 1919, 14, 271).

Magnesium oxide. *Magnesia.* MgO. This is the product of the combustion of magnesium in air or oxygen. It is also formed when the carbonate or nitrate is heated in the air. As thus obtained, it is a white amorphous powder, but may be obtained crystallised in cubes and octahedra by heating the amorphous form in a current of hydrogen chloride. If ferric oxide be mixed with the magnesia, brilliant black octahedra of magnoferrite $MgO{\cdot}F_2O_3$ are formed, together with octahedra of MgO, slightly yellow in colour, due to oxide of iron, and identical with those of *periclase*, a mineral found at Monte Somma, near Vesuvius. Moissan obtained transparent crystals of magnesia, sp.gr. 3·654, by distillation of the oxide in the electric furnace. Ordinary magnesia is known in commerce as *magnesia usta* or calcined magnesia, and is much used for medicinal purposes. It is a fine bulky powder of sp.gr. 3·07 to 3·2. The sp gr. is increased to 3·61 by heating in a pottery furnace.

It melts at 2800° (Kanolt, J. Franklin Inst. 1913, 176, 587), and on solidifying forms a hard enamel, which scratches glass. It is alkaline to litmus, but is not caustic. It is almost insoluble in water; according to Fresenius, it requires 55,368 parts of either cold or boiling water to effect solution. This solution has an alkaline reaction. Magnesia containing 0·1 p.c. of chromic oxide becomes slightly fluorescent after ignition.

Manufacture.—Magnesia is generally obtained commercially by gentle but prolonged heating of the carbonate or by heating the hydroxide. Since the discovery, however, of the immense stores of carnallite, the double chloride of potassium and magnesium, in the saline deposits of Stassfurt, several processes have been patented for utilising the waste magnesium chloride liquor obtained as by-product in the manufacture of potassium chloride.

Schlœsing, in 1881 (Compt. rend. 93, 156, 215), describes the following process for obtaining cheap magnesia. A paste of slaked lime and water containing 34–36 p.c. of calcium oxide is allowed to run through perforations in a metallic plate into a solution of magnesium chloride containing 60–95 grams per litre. As soon as the lime paste reaches the solution it becomes coated with a layer of magnesium hydroxide, which acts like a shell, causing it to form long threads, which are entirely converted into magnesium hydroxide in about 6 days. The hydroxide thus obtained may be washed by diffusion, and, when triturated with water and dried, gives a compact, friable powder, which can of course be converted into calcined magnesia by heating in a suitable furnace. Presence of common salt has no effect on the process, but if soluble sulphates are present, they must be removed by adding some of the calcium chloride solution from a previous operation, allowing to settle, and decanting from the more insoluble calcium sulphate.

Ramdohr, Blumenthal, & Co., in 1881, patented the following process (D. R. P. 19259, Sept. 1881). A solution of magnesium chloride is evaporated until it consists approximately of $MgCl_2,6H_2O$. About 4–10 p c. of magnesite is added, and the mixture heated to redness in a current of air until the evolution of hydrogen chloride ceases. Magnesium oxychloride is left, which, on heating with water, splits up into magnesium hydroxide and chloride

The United Chemical Works Joint Stock Co., Leopoldshall, in 1882, patented the following process (D. R. P. 20277, Feb. 1882). Burnt lime is treated with a solution of calcium chloride. After removal of the clear liquid the paste is washed with a fresh solution of calcium chloride, whilst the clear solution in turn is repeatedly digested with fresh lime. A small portion of this solution is then mixed with the magnesium chloride solution in order to precipitate all the iron and sulphuric acid which it contains The purified magnesium solution is then added to the bulk of the clear calcium solution, which contains calcium oxychloride $3CaO{\cdot}CaCl_2,16H_2O$, when pure hydrated magnesium oxide separates out.

According to Meunier (Bull. Soc. Chim. 1919, 25, 560) magnesia may be freed from lime by igniting at a red heat and after cooling extracting with successive portions of a 10 p.c solution of sucrose until the extract gives no turbidity with ammonium oxalate.

On account of its infusibility, magnesia is now extensively used in the manufacture of firebricks, especially for use in the basic Bessemer steel process. The bricks are made of crushed dead-burnt magnesite mixed with sufficient gently calcined magnesite to give plasticity to the paste formed by mixing the materials with water to permit of moulding. The bricks are fired at a red heat before use.

A kiln described before the Ceramic Society, 1918, for the dead burning of magnesite shows a considerable advance on the older types, both for fuel economy and increased output. The kiln consists of one vertical chamber without contraction at the hot zone. The hottest zone is lined with magnesite bricks and other parts with best firebrick; the whole having a backing of secondary firebricks. The material is raised by an electric lift and dropped into a charging bell. It gradually descends through the dead burning zone to the cooling region, at the bottom of which it is automatically pushed out into a discharging hopper. The whole process takes about 40 hours, including 3 hours in the dead burning zone. Air for combustion is supplied by a fan through six damper-controlled openings at the bottom, and passes upward through the burnt material, becoming very hot by the time it reaches the level of the gas inlets. A secondary system of air flues constructed in the brickwork (which heat the air) conveys air about two-thirds up the kiln and then downwards again to enter through slits just above the gas ports; these are only used as necessity arises. The gas is generated in a gas producer, and is heated by passing through three flues before it enters through the six ports. With good English coal a temperature of 1700° is attained. The ascending gases leave the kiln at 150°, a suction fan being used to exhaust the gases. The mechanical arrangements of the draughts and process of calcination give complete control. A special feature of the kiln is the rotating bottom, consisting of a conical cast-steel head with ribs on the upper surface carried on a vertical shaft. Its rotation moves the finished material towards the opening and tends to grind any lumps in the calcined product, also, by keeping the column in constant motion, it causes the material to descend gradually. The shaft rotates once in 40 minutes and the wear is very slight (Engineering, 1918, p. 619).

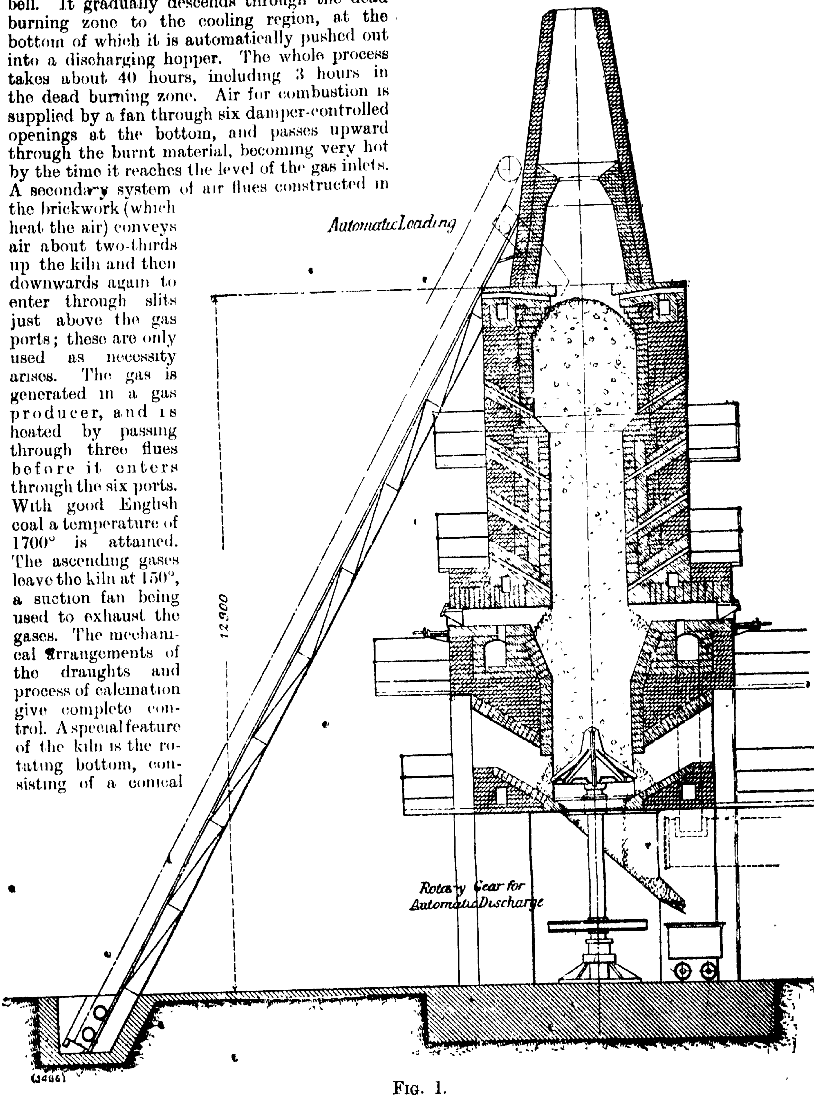


FIG. 1.

(*From* 'Engineering.')

Magnesia bricks with high magnesia content, tested by resistance to crushing with increasing temperature, showed a sudden fall between 1500° and 1600°; less pure varieties showed a fall between 1300° and 1400° as compared with 1100° for ferro-chrome brick (Compt. rend. 1917, 165, 488).

Dolomite has also been extensively used for the preparation of magnesia for refractories. Closson's plan was to mix calcined dolomite with a solution of magnesium chloride, when calcium chloride and magnesia are formed; the calcium chloride can then be washed out. Magnesia may be obtained from dolomite by calcination at 900° and treatment of the solution obtained by lixiviation by ammonium and sodium chlorides, the ammonia being recovered and magnesium hydroxide precipitated by calcined dolomite (U.S. Pat. 1156662, 1915). Many other wet methods for the recovery of magnesia have been employed, but, according to Wedding, magnesia prepared in the wet way, though obtained from cheap waste materials or by-products, is too expensive for the manufacture of bricks.

Magnesia, in combination with lime, also finds an extended use for mortar making in districts where only magnesium limestone is available. The dolomitic limestone is burnt at a lower temperature than ordinary limestone, otherwise its hydrating properties and consequently the quality of the mortar are impaired.

Magnesium suboxide. A substance of this nature appears to be formed when a solution of sodium or ammonium chlorides is electrolysed, using poles of magnesium wire, the positive pole becoming covered with a black deposit (Beetz, J. 1866, 172). The same substance is also obtained when magnesium is immersed in solutions of chlorides of the alkalis and alkaline earths, common salt giving the largest deposit. In a few days it disappears, being replaced by the ordinary white oxide. It turns white when heated just below redness. It dissolves in nitric acid with partial reduction of the acid. It readily dissolves in hydrochloric and sulphuric acids with effervescence, forming the ordinary chloride and sulphate (Gore, Chem. News, 50, 157).

It is also obtained as a dark brown substance when chlorides of magnesium and potassium are electrolysed. It is without action on a solution of nickel chloride in absolute alcohol (metallic magnesium precipitates nickel). It decomposes water evolving hydrogen. It is not formed if oxygen is completely excluded from the electrolyte (Trans. Amer. Electrochem. Soc. 27, 209).

Magnesium hydroxide $Mg(OH)_2$ occurs native as the mineral *brucite*, crystallising in the rhombohedral section of the hexagonal system. The hydroxide is precipitated as a white powder when the hydroxide of potassium or sodium is added to the solution of a magnesium salt. De Schulten (Compt. rend. 101, 72) obtained it in the form of flattened hexagonal prisms, of sp.gr. 2·36 at 15°, by heating a mixture of 12 grams crystallised magnesium chloride $MgCl_2,6H_2O$, 340 grams of potash, and 60 c.c. of water, at 210°–220°. The solid residue, after washing away the alkali, consisted of these small crystals of the hydroxide. They were readily soluble in acids and in a warm solution of ammonium chloride.

Magnesium hydroxide slowly absorbs carbon dioxide from the air. At a low red heat it loses its water, becoming converted into the oxide. This calcined magnesia is again capable of taking up water, with evolution of heat, to reform the hydroxide, provided that it has not been too strongly heated Magnesium oxide obtained by igniting magnesite at 1450° was only hydrated to the extent of 70 p.c. in 6 years.

Magnesium hydroxide is much used upon the Continent for extracting sugar from molasses; it forms an insoluble granular crystalline magnesium saccharate, which when decomposed by carbon dioxide yields pure sugar.

In order to meet this demand, the Consolidated Alkali Company of Stassfurt manufacture large quantities of magnesium hydroxide by the following process. The 3 p.c. of sulphates contained in the last mother liquor from the extraction of potassium chloride from carnallite are first removed by means of a solution of calcium chloride. A quantity of milk of lime is then added rather less than sufficient to decompose the whole of the magnesium chloride; the precipitated magnesia is allowed to settle and then passed through filter presses, in which it is thoroughly washed. The magnesium hydroxide thus obtained contains only 0·1 p.c. of calcium sulphate, and is eminently suitable for the purpose of the sugar refiner (Hake, J. Soc. Chem. Ind. 2, 149).

Magnesia prepared by heating the nitrate is converted by prolonged immersion in water into a form of the hydroxide having the density of marble, but harder and more translucent. A similar form, but contaminated with oxide of iron and aluminium, magnesium carbonate and sand, is also obtained by action of water upon the product of the ignition of commercial magnesium chloride. This singular property of hardening is only possessed by magnesia prepared by ignition of the nitrate or chloride at a moderate red heat. After heating to whiteness it appears to lose it. Ignition of native magnesite at the lowest possible temperature also yields a product possessing the same hydraulic property, but the basic carbonates of commerce yield a perfectly soft hydroxide. The paste prepared from calcined magnesite and water hardens in about half a day, and afterwards not only withstands the action of water, but actually acquires in contact with it the hardness of the best Portland cement.

A mixture of magnesia with a concentrated solution of magnesium chloride of sp gr. 1·16–1·26 hardens in a short time to a compact mass of basic chloride, which resists the action of water. The pasty mixture is very plastic, and is capable of binding more than twenty times its weight of sand.

Magnesium chloride $MgCl_2$ is one of the salts present in sea-water and in the water of many springs. It also occurs combined with potassium chloride in large quantities as the mineral *carnallite* $MgCl_2{\cdot}KCl,6H_2O$ in the Stassfurt deposits. It is formed when magnesium burns in chlorine, or when a stream of chlorine is passed over a heated mixture of magnesia and carbon. It is also produced by dissolving the metal, oxide, or carbonate, in hydrochloric acid. On concentration of the solution monoclinic crystals of the composition $MgCl_2,6H_2O$ separate out. Crystals of this composition have also been discovered, associated with carnallite and rock salt, at Stassfurt, and named *bischofite*. On attempting to obtain the anhydrous chloride by ignition of these crystals, hydrochloric acid is evolved in addition to water, and a portion of the chloride becomes converted to oxide. If, however, the crystals be heated in a current of hydrogen chloride, the anhydrous chloride is obtained without the formation of any basic salt (Hempel, Ber. 21, 897). Another method of obtaining the anhydrous chloride is to add ammonium chloride to the solution, evaporate to dryness, and ignite in a platinum dish The magnesium ammonium chloride thus formed loses its water without any decomposition of the magnesium chloride, and the ammonium chloride can then be sublimed out, leaving the anhydrous magnesium chloride as a clear fused mass, which on cooling solidifies to a crystalline solid. Magnesium chloride is a solvent for the crystallisation of metallic oxides. Octahedral crystals of 'magnesia-red' can be obtained by heating $MgCl_2$ with cobalt sulphate. By a similar process, nickel sulphate gives rise to octahedral crystals of 'magnesia green.' The crystals are a mixture of the two oxides. 100 parts of water at 0° dissolve 52·2 parts of the anhydrous chloride, with considerable evolution of heat, forming a solution of sp.gr. 1·3619 at 15° (Engel, Bull. Soc. chim. [ii.] 47, 318). At the ordinary temperature 100 parts of water dissolve about 130 parts, and at 100° about 366 parts. This solution on cooling again deposits the crystals. Magnesium chloride solution possesses a bitter taste. The solid, either anhydrous or crystals, is very deliquescent. It combines directly, with evolution of heat, with methyl and ethyl alcohols, the solutions yielding, on cooling with ice, crystals of $MgCl_2,6CH_3OH$ and $MgCl_2,6C_2H_2OH$, respectively.

Commercial preparation.- The last mother liquor obtained in the process of preparing potassium chloride from the carnallite at Stassfurt supplies as by-product large quantities of magnesium chloride. The liquor has a sp.gr. of 1·32, and contains no less than 35 p.c. of the chloride. It is first evaporated to sp gr. 1·34, when potassium and sodium chlorides and magnesium sulphate separate out. The hot concentrated liquor is then run into casks, where on cooling it solidifies to a white translucent mass containing 50 p.c. of magnesium chloride. In this state it is largely exported to this country, being used by cotton-spinners as a thread lubricator (Hake, J. Soc. Chem. Ind. 2, 149).

Lanquetin, in 1881, patented (D. R. P. 20396) a process for preparing magnesium chloride by introducing burnt magnesite or dolomite into a solution of waste calcium chloride, and driving carbon dioxide through the mixture, when calcium carbonate separates out and magnesium chloride remains in solution.

Cochrane and Bramley, of Middlesbrough (Eng. Pat. 15498, Nov. 1886), charge hydrated magnesium carbonate into a series of closed vessels through which a solution of calcium chloride is circulated, carbon dioxide being at the same time injected. Magnesium chloride is in this case gradually formed in solution and calcium carbonate precipitated.

Magnesium chloride may also be extracted from the mother liquor of the potassium chlorate manufacture (Muspratt and Eschellmann, Widnes, Eng. Pat. 1900, Feb. 1885).

Magnesium chloride unites with the alkaline chlorides to form crystalline double salts.

Magnesium chloride solution is preferable to brine as a refrigerating medium. As it is more viscous than brine it is less liable to spray or splash, and its freezing point is lower than brine of the same concentration.

Magnesium potassium chloride

$$MgCl_2·KCl,6H_2O$$

the carnallite of Stassfurt, crystallises in colourless deliquescent rhombic prisms. On heating, the water is driven off without loss of chlorine, the anhydrous mixture fusing at a red heat. The native carnallite used at Stassfurt for the extraction of potassium and magnesium chlorides has the following average composition (Hake, J Soc. Chem. Ind. 2, 149):

KCl . .	16·2	$CaCl_2$ . .	0·2
$MgCl_2$ . .	24·3	Clay and $CaCO_3$	2·1
$MgSO_4$. .	9·7	H_2O . .	28·8
$NaCl$ . .	18·7		

Magnesium ammonium chloride

$$MgCl_2·NH_4Cl,6H_2O$$

is deposited from mixed solutions of magnesium and ammonium chlorides in small rhombic crystals.

The corresponding sodium salt appears to contain only one molecule of water (Poggiale, Compt. rend 20, 1130).

Magnesium calcium chloride, *Tachydrite*, $2MgCl_2·CaCl_2,12H_2O$, is also found at Stassfurt in deliquescent yellowish masses.

Magnesium oxychlorides. When highly calcined magnesia is treated with a strong solution of magnesium chloride, it dries in a few hours to a hard mass of oxychloride, capable of receiving a polish. A sample prepared in this manner, and hardened by 6 months' exposure in the air, was found to consist of a mixture of $MgCO_3$ with a compound

$$MgCl_2·5MgO,17H_2O$$

On heating to 180° it was converted into $MgCl_2·5MgO,6H_2O$. By prolonged treatment with water the whole of the magnesium chloride was extracted, and the compound $2MgO·3H_2O$ left. This residual hydrate is a compact solid as hard as sandstone, possessing a brilliant surface, and taking a high polish; its cohesive power is not impaired by either cold or hot water (Bender, Annalen, 159, 341).

Magnesium oxychloride is the essential constituent in Sorel cement, usually made by adding a solution of magnesium chloride to finely ground calcined magnesite; when mixed with various filling materials, such as wood flour, cork, talc, silica, asbestos, clay, marble dust, or sand, it is frequently used in the construction of 'sanitary flooring.' It was stated that magnesia cement was used by the Germans for gun emplacements, as it sets quickly, produces a smooth, even floor, which may be laid in large areas without cracking, and attains great strength sooner than Portland cement.

The crystalline deposit frequently found in bottles containing magnesia mixture (magnesium sulphate or chloride, ammonia and ammonium chloride) consists of a hydrated oxychloride $MgCl_2·5MgO,13H_2O$. On washing the crystals with a large quantity of water the whole of the chloride may be removed, the residue consisting of hydrated oxide (Davis, Chem. News, 25, 258).

By mixing freshly calcined magnesia with a solution of magnesium chloride in a flask well corked and nearly filled with the liquid, and heating on a water-bath with frequent agitation, needle-shaped crystals of an oxychloride are formed. When washed and dried at 110° they consist of $MgCl_2 \cdot 10MgO,14H_2O$. The dry crystals are not attacked by carbon dioxide, but when moist are decomposed (Krause, Annalen, 165, 38).

When 20 grams of calcined magnesia are boiled with a solution of 400 grams magnesium chloride in 500 grams of water and the solution filtered, the filtrate deposits needles of $MgCl_2 \cdot MgO,16H_2O$. When dried *in vacuó* they are converted into $MgCl_2 \cdot MgO,6H_2O$. Both salts are decomposed by water and alcohol (André, Compt. rend. 91, 444).

When crystallised magnesium chloride is heated in air, an oxychloride of variable composition appears to be left, a portion of the chlorine passing away in the form of hydrochloric acid. If the chloride be heated to a sufficiently high temperature in a current of air a certain amount of free chlorine is evolved; and if a mixture of hydrogen chloride and air is passed over the heated chloride, especially in presence of a little free magnesia, a larger quantity of chlorine is obtained in the free state. This reaction forms the basis of the Weldon-Pechiney process of manufacturing chlorine, as worked at Salindres (Weldon, Eng. Pat. 9307, June, 1884; 11036, Aug. 1884). A solution of magnesium chloride is first evaporated down until it consists approximately of $MgCl_2,6H_2O$. This is then converted to oxychloride by addition of 1¼ equivalents of calcined magnesia. This oxychloride is crushed and sifted, solid pieces free from dust being eventually chosen not larger than the size of a walnut. It is next heated to remove a portion of its water, and finally decomposed by heating to a high temperature in a current of air. The furnace employed for the latter process is constructed upon the principle of a baker's oven. It consists of a series of vertical chambers, the thickness of the dividing walls of which is greater than the width of the spaces between them. Before charging these spaces with the small lumps of oxychloride, products of combustion are passed through them until the dividing walls are raised to a high temperature. After charging, the oxychloride becomes heated by contact with the walls, and a mixture of chlorine, nitrogen, excess of air, and hydrogen chloride is evolved. The hydrochloric acid is condensed in ordinary towers, and the remaining gases pass on to the bleaching powder chambers. The magnesium remains as oxide, the oxygen being furnished by a regulated supply of air, and is afterwards partly dissolved in the condensed hydrochloric acid for preparation of more oxychloride (Weldon, J. Soc. Chem. Ind. 4, 175). The reactions occurring in the process are probably as follows:

(1) $H_2O+MgCl_2=MgO+2HCl$.

(2) $2HCl+O=H_2O+Cl_2$.

(3) $MgCl_2+O=MgO+Cl_2$.

(Kingzett, J. Soc. Chem. Ind. 7, 286).

Nithack (D. R. P. May 29, 1884) decomposes magnesium chloride for the preparation of chlorine by injecting a fine spray of the solution into heated chambers, when the same reactions occur.

Mond (Brit. Assoc. 1896, 741) modified the process for recovering both ammonia and chlorine from the ammonium chloride produced in the ammonia soda process. Magnesia is mixed with a little china clay and potassium chloride to facilitate the production of a perfectly anhydrous chloride. The mixture is made into pills and placed in towers. These are heated from a previous operation to 300°; the ammonium chloride vapour is passed through, producing ammonia and magnesium chloride. Air at 600° is then circulated, when free chlorine is liberated and magnesia reformed. Hence the process becomes continuous.

Hermite (J. Soc. Chem. Ind. 7, 726, 737) prepares chlorine for bleaching purposes by the electrolysis of a solution of magnesium chloride.

Magnesium bromide $MgBr_2$ (m.p. 711°) occurs in sea-water and many salt springs. It resembles the chloride, being deposited from a solution of magnesia in hydrobromic acid in needles of $MgBr_2,6H_2O$, which behave like the chloride on heating.

Magnesium iodide MgI_2 also occurs in sea-water and saline springs, and may be obtained by dissolving magnesia in hydriodic acid, when deliquescent crystals separate, which readily evolve iodine on warming.

Magnesium fluoride MgF_2 occurs native in the mineral *sellaite* in colourless quadratic crystals, and may be prepared in an amorphous form by evaporating magnesia with excess of hydrofluoric acid. When the amorphous form is fused with sodium chloride and gradually cooled, it is obtained, after washing with water, in crystals resembling those of sellaite

Feldmann (Eng. Pat. 15295, Nov. 1887) patented a process for an industrial preparation of this salt Magnesium chloride is treated with calcium fluoride in either the dry or the wet way. In the former the fluorspar is mixed with the anhydrous chloride in excess, and the mixture fused at a red heat, when $CaCl_2$ and MgF_2 are formed. After cooling, the mass is lixiviated, when the magnesium fluoride remains behind. In the wet method powdered fluorspar is suspended in a concentrated solution of magnesium chloride and heated till double decomposition occurs, water being added to make up the loss by evaporation. It is then allowed to cool, when the mass solidifies and is lixiviated as before. Any undecomposed calcium fluoride may be removed by elutriation from the specifically lighter magnesium fluoride.

A double fluoride of magnesium and sodium $MgF_2 \cdot NaF$ is obtained in insoluble cubical crystals by fusing magnesium chloride with a large excess of sodium fluoride and chloride and allowing to cool slowly. Also in the amorphous state by boiling a solution of sodium fluoride with magnesia.

Magnesium carbide has not been isolated in the pure state. It is obtained mixed with carbon by heating magnesium powder to redness in the vapour of benzene (Parkinson) or acetylene (Berthelot). According to Moissan, it is completely decomposed in the electric furnace, which explains why magnesia can be fused in a carbon crucible without reaction (Ann. Chim. Phys. [vii.] 16, 151).

Novák (Zeitsch. physikal Chem. 73, 513) obtained the carbide by heating magnesium in a tube at a definite constant temperature and passing over it a definite volume of a gaseous hydrocarbon. He obtained two carbides, MgC_2 and Mg_2C_3, and their decomposition with water proceeds according to the equations

$$MgC_2+2H_2O=Mg(OH)_2+C_2H_2$$
$$Mg_2C_3+4H_2O=2Mg(OH)_2+C_3H_4$$

The formation of MgC_2 by acetylene commences at 400°C. At 460° the presence of Mg_2C_3 in the product can be proved and the proportion increases up to 545°.

Magnesium carbonate $MgCO_3$ occurs native as *magnesite* in rhombohedral crystals isomorphous with those of calcite. It is also found in large compact or granular masses, and, associated with calcium carbonate, as *dolomite* $(MgCa)CO_3$, in immense quantities all over the world. The amorphous precipitate formed when an alkaline carbonate is added to a solution of a magnesium salt has the composition

$$MgCO_3,2H_2O$$

but after standing an hour or two at a temperature below 16°, it becomes converted into tabular crystals of $MgCO_3,5H_2O$. If the temperature exceeds 22° it beomes converted into prismatic crystals of $MgCO_3,3H_2O$. Between 16° and 22° both these hydrates are formed. The amorphous precipitate is, decomposed by water into a basic carbonate of the composition

$$5MgO\,4CO_2,11H_2O$$

or $5(MgCO_3,2H_2O)$, in which one molecule of $MgCO_3$ has been converted into $Mg(OH)_2$. This basic carbonate absorbs carbon dioxide from the air, and becomes $MgCO_3,2H_2O$ again (Engel, Compt. rend. 100, 911). According to Marignac, normal magnesium carbonate is also formed by the action of magnesium chloride on calcium carbonate.

When the precipitated carbonate is suspended in water and dissolved by the passage of a current of carbon dioxide, on evaporation of the solution the anhydrous carbonate is precipitated in minute crystals isomorphous with aragonite, the rhombic form of calcium carbonate. On the other hand, when mixed solutions of a soluble magnesium salt and an alkaline bicarbonate supersaturated with carbon dioxide are inclosed in a strong vessel closed by a cork, through which the carbon dioxide is slowly allowed to escape, microscopic rhombohedrons of the anhydrous carbonate resembling those of native magnesite and calcite are deposited.

Both the natural and artificial varieties of magnesium carbonate give an alkaline reaction with litmus solution. They dissolve slowly in acids with but little effervescence.

Magnesium carbonate dissolves in water saturated with carbon dioxide. According to Engel (Compt. rend. 100, 444, 1224) the solubility at constant temperature is proportional to the cube-root of the pressure of the carbon dioxide. The results of a large number of experiments agreed with those calculated from the general formula $x^{0\cdot333}=ky$ or $y=\frac{1}{k}\sqrt{x}$, where x represents the pressure of carbon dioxide, y the quantity dissolved, and k a constant $=0\cdot03814$. At different temperatures under atmospheric pressure the amount of magnesium carbonate dissolved is proportional to the coefficient of solubility of carbon dioxide at the particular temperature. The following table is given by Engel and Ville (Compt. rend. 93, 340) showing the solubility first at constant temperature and second at constant pressure :

Atmospheres pressure	Temperature	$MgCO_3$ dissolved in a litre of water
	°	
1·0	19·5	25·79
2·1	19·5	33·11
3·2	19·7	37·30
4·7	19·0	43·50
5·6	19·2	46·20
6·2	19·2	48·51
7·5	19·5	51·20
9·0	18·7	56·59
mm. pressure		
751	13·4	28·45
763	19·5	25·79
762	29 3	21·94
764	46·0	15·70
764	62·0	10·35
765	70·0	8·10
765	82·0	4·90
765	90·0	2·40
765	100·0	0·00

When the solution in carbonic acid is left to evaporate spontaneously, or kept in a partially closed flask for some time at 50°, it deposits small hexagonal prisms of $MgCO_3,3H_2O$, which effloresce in air, becoming opaque. At a winter temperature the same solution deposits monoclinic prisms of $MgCO_3,5H_2O$. Warmed with water at 50°, they are converted into the trihydrate, whilst on boiling with water they lose carbonic acid and become converted eventually into the basic carbonate

$$2MgCO_3\cdot Mg(OH)_2,2H_2O.$$

Saturated solutions of magnesium hydrogen carbonate deposit between 65° and the boiling point a basic carbonate, $4MgO,3CO_2.6H_2O$, in the form of slender needles. Between 65° and 55°, the basic carbonate separates, mixed with the trihydrate, $MgCO_3,3H_2O$, below 55°, the trihydrate alone is formed down to about 6°, and at 2° the unstable pentahydrate is formed (Leitmeier, Z. Kryst. Min. 1909, 47, 104).

Basic carbonates. A basic carbonate of the composition $3MgCO_3\cdot Mg(OH)_2,3H_2O$ occurs native as *hydromagnesite* in small white monoclinic crystals of sp.gr. 2·14–2·18. A salt of the same composition is also obtained by mixing magnesium sulphate with excess of a hot solution of potassium carbonate and boiling the precipitate with fresh quantities of water so long as acid carbonate dissolves out. Also by boiling a saturated solution of the acid carbonate, and twice boiling the precipitate produced with fresh quantities of water. When dried at 100° in the air it absorbs carbon dioxide, and is converted into $5MgO\cdot4CO_2,5H_2O$.

Another basic carbonate of the composition $2MgCO_3\cdot Mg(OH)_2,2H_2O$ is obtained as above from the solution of the normal carbonate in carbonic acid. Also, according to Fritzsche (Pogg. Ann. 37, 310), by precipitating magnesium sulphate with a very large excess of sodium carbonate and boiling till granular, then washing rapidly three times with fresh boiling water.

Commercial carbonates. The commercial preparation known as *magnesia alba* is a basic carbonate of slightly varying composition, according to the conditions of production. It is usually prepared by precipitation of either the commercial sulphate or chloride of magnesium with sodium carbonate. As thus obtained it is a very light bulky powder, and is distinguished as *magnesia alba levis.* If the precipitation is carried on at a higher temperature by the addition of one volume of a cold saturated solution of sodium carbonate to a boiling mixture of one volume of a saturated solution of magnesium sulphate with thirty volumes of water, the precipitate washed with hot water and dried at 100°, a denser form is obtained known as *magnesia alba ponderosa.* The composition of the light variety is generally given as the same as that of hydromagnesite

$$5MgCO_3{\cdot}Mg(OH)_2,3H_2O$$

Beckurts (Arch. Pharm. [iii.] 18, 429; 19, 13), however, deduces the formula

$$5MgCO_3{\cdot}2Mg(OH)_2,7H_2O$$

but also found several specimens of the hydromagnesite formula, but containing $4H_2O$. Kraut (Arch. Pharm. [iii.] 20, 180) gives

$$4MgCO_3{\cdot}Mg(OH)_2$$

as the correct formula. Hence it appears likely that different samples vary somewhat in composition. As representing the composition of the heavy variety, Beckurts (*l.c.*) gives the formula $3MgCO_3,Mg(OH)_2,4H_2O$, which only differs from that of hydromagnesite by one molecule of water.

Magnesia alba levis and *ponderosa* yield upon calcination corresponding light and heavy varieties of the oxide, known in commerce as *magnesia usta levis* and *magnesia usta ponderosa.*

Another method of preparing *magnesia alba* was patented by Pattinson. This consists in treating slightly ignited dolomite with water and carbon dioxide under a pressure of 5-6 atmospheres. So long as any magnesium carbonate remains undissolved, the calcium carbonate is unattacked, the acid magnesium carbonate being much more readily formed. This solution of hydrogen magnesium carbonate is decanted from the calcium carbonate and heated by injection of steam, when *magnesia alba* is precipitated as a white bulky powder of loose texture. Unignited dolomite does not yield any acid carbonate with carbonic acid.

Bramley and Cochrane, of Middlesbrough, patented a process (Eng. Pat. 13762, Oct. 1886) in which magnesia is added to the solution of an alkaline bicarbonate or sesquicarbonate and the mixture heated and agitated. The alkaline carbonate is converted to a normal carbonate, and hydrated magnesium carbonate formed. The operation is performed in closed vessels to prevent loss of carbon dioxide.

Magnesia alba can also be profitably prepared from sea-water (Gutzkow, Dingl. poly. J. 270, 30). The mother-liquor (bittern) obtained after extraction of common salt (bay-salt) is treated with milk of lime; the precipitated magnesium hydroxide is allowed to settle, the supernatant liquid removed by decantation, and the precipitate stirred up with water through which a stream of carbon dioxide is passed. The hydroxide is dissolved as acid carbonate. The clear solution is then heated rapidly to 70°, and afterwards more gradually to the boiling-point. The precipitated *magnesia alba* is filtered off and dried on plates heated by steam. If necessary, the original mother-liquor may first be freed from organic matter by treatment with alum.

Magnesia alba is almost insoluble in water, but dissolves readily in solutions of ammonium salts owing to the formation of soluble double salts of magnesium and ammonium and ammonium carbonate.

Magnesium ammonium carbonate

$$MgCO_3{\cdot}(NH_4)_2CO_3,4H_2O$$

separates in rhombohedral crystals from a mixture of cold aqueous solutions of magnesium sulphate or chloride and excess of ammonium carbonate and free ammonia.

Magnesium potassium carbonate

$$MgCO_3{\cdot}K_2CO_3,4H_2O$$

is obtained in small rhombic prisms when *magnesia alba* is digested with a solution of acid potassium carbonate for 15 hours at 60°–70°.

A salt of the composition

$$MgCO_3{\cdot}HKCO_3,4H_2O$$

is obtained in large crystals from a cold aqueous mixture of magnesium chloride or nitrate with excess of acid potassium carbonate. Engel (Compt. rend. 100, 1224) obtained the same salt by decomposing a solution of the acid magnesium carbonate with potassium bicarbonate, and also by direct action of the potassium bicarbonate upon normal magnesium carbonate.

Magnesium sodium carbonate $MgCO_3{\cdot}Na_2CO_3$ is similarly obtained in small anhydrous crystals by digesting *magnesia alba* with sodium bicarbonate.

Magnesium nitride Mg_3N_2. Magnesium combines directly with nitrogen when heated to redness. It is also one of the products of the incomplete combustion of magnesium in air. Matignon (Compt. rend. 1912, 154, 63) states that oxygen is absorbed at a temperature of 600° and nitrogen at 670°. At the latter temperature and atmospheric pressure, oxygen is absorbed at least 1000 times more rapidly than nitrogen. The nitride is conveniently obtained by the interaction of finely divided magnesium and ammonia. From the heat developed when the nitride is decomposed by dilute sulphuric acid the heat of formation is calculated to be +119·7 cals. It is a greenish-yellow amorphous body which decomposes slowly in humid air, yielding ammonia and magnesia, rapidly in contact with water with elevation of temperature. Hydrochloric and nitric acids decompose it yielding ammonia and the magnesium salt. With sulphuric acid it yields sulphur dioxide and magnesium sulphate. Argon does not combine with magnesium.

Magnesium amide. Anhydrous liquid ammonia dissolves magnesium to a slight extent, producing a blue solution which decomposes gradually with the formation of the amide and the liberation of hydrogen.

Mixtures of liquid ammonia and acetylene react with metallic magnesium at the ordinary temperature, and on evaporation of the solution the crystalline compound $MgC_2,C_2H_2,5NH_3$ is obtained together with ethylene and a small quantity of ethane. At atmospheric pressure this compound loses a portion of its ammonia when the temperature reaches 2° and is converted into the compound $2MgC_2,2C_2H_2,7NH_3$ which is stable up to 60° at which temperature acetylene and ammonia are given off, leaving a residue consisting of magnesium amide and nitride, together with a little carbide (J. Phys. Chem. 18, 85). Potassium ammono-magnesiate is obtained by the action of potassamide on magnesium amide in liquid ammonia solution (J. Amer. Chem. Soc. 37, 2295).

Magnesium nitrate ($Mg(NO_3)_2$ occurs in the mother-liquors of the saltpetre manufacture, and also frequently in well-water. It may readily be prepared by dissolving *magnesia alba* in nitric acid and evaporating to small bulk, when monoclinic prisms and needles of the hydrated salt $Mg(NO_3)_2,6H_2O$ separate out. These are soluble in half their weight of cold water, and also in nine times their weight of alcohol of sp.gr. 0·84, with which magnesium nitrate forms an alcoholate of the composition $Mg(NO_3)_2,6C_2H_6O$. When dried over sulphuric acid the hydrated salt loses four molecules of its water, and at the temperature of melting lead another molecule is evolved, leaving the salt $Mg(NO_3)_2,H_2O$. When this latter salt is heated to a still higher temperature the last molecule of water is given off, together with part of the nitric acid, and a tri-magnesium nitrate $Mg_3(NO_4)_2$, analogous to the tri-orthophosphate, is left.

Magnesium borate. When magnesium oxide in slight excess is heated with a mixture of boric anhydride and potassium hydrogen fluoride in molecular proportions, the borate $3MgO,B_2O_3$ is obtained in transparent acicular crystals which are soluble in inorganic acids but not in acetic acid or water.

Magnesium phosphide Mg_3P_2 may be obtained by heating magnesium filings with red phosphorus (Parkinson) or by passing phosphorus vapour over magnesium filings, heated to redness, in a current of carbon dioxide. Gautier obtained it crystalline by heating red phosphorus and magnesium in a graphite boat, then driving off the excess of phosphorus in a current of hydrogen (Compt. rend. 128, 1167). It decomposes water, yielding phosphoretted hydrogen and magnesium hydroxide.

Tri-magnesium orthophosphate $Mg_3(PO_4)_2$ is found in the ashes of plants and animals and combined with fluorine occurs in nature as *wagnerite* $Mg(MgF)PO_4$. It may be prepared by adding magnesium sulphate in excess to a solution of trisodium phosphate and boiling. It is a white amorphous powder containing $5H_2O$, which on calcining loses water and becomes phosphorescent.

Di-magnesium orthophosphate $Mg_2H_2(PO_4)_2$ is formed by precipitating a solution of a magnesium salt with normal sodium phosphate. If the solution is dilute it separates in hexagonal needles containing seven molecules of water. It occurs in the fæces of man (*cf.* Balareff, Zeitsch. anorg. Chem. 1918, 102, 241).

Ammonium magnesium phosphate

$$MgNH_4PO_4,6H_2O$$

is formed as a crystalline precipitate when sodium phosphate is added to an ammoniacal solution of a magnesium salt. The precipitate is almost insoluble in water and still less so in ammonia. It serves for the quantitative estimation of both magnesia and phosphoric acid. The compound occurs in nature in well-formed crystals known under the name of *struvite*.

Magnesium pyrophosphate $Mg_2P_2O_7$ is obtained by igniting either ammonium magnesium phosphate or the acid phosphate.

Magnesium sulphide MgS is formed by heating magnesium filings in the vapour of sulphur or sulphuretted hydrogen. So obtained it is a grey amorphous material which is difficultly fusible even in the electric furnace (Mourlot, Compt. rend. 127, 180). Tiede (Ber. 1916, 49, 1745) states that the sulphide prepared by the method of Mourlot contains only 8 p.c. of sulphur. Reichels' process of heating magnesium in a current of hydrogen followed by hydrogen mixed with sulphur gave a product containing 30 to 50 p.c. sulphur. This was purified by heating it in a highly evacuated quartz tube to 600°–700° for two hours, when the excess of metal volatilised. It was also obtained by boiling the crude sulphide (10 grams) with fresh absolute ether (100 c.c.), ethyl iodide (19 grams), and a crystal of iodine for three hours, moisture being rigorously excluded. The metal dissolves in the alkyl iodide whilst the sulphide is unaffected. The purified sulphide was washed with ether and dried in a vacuum.

It is an amorphous powder of reddish-white colour and feebly luminescent after exposure to daylight or the arc light. Luminosity is best excited by rays of long wave length. Radium, X-, and ultra-violet rays did not excite it. When exposed to cathode rays magnesium sulphide shows a bright blue and red fluorescence with a feeble after-glow. Magnesium sulphide containing bismuth exhibits an intensely blue phosphorescence which is excited by daylight or arc or mercury-vapour light. Specimens containing antimony have a delicate yellow colour and a persistent, intensely yellow-green phosphorescence after excitation by daylight or particularly by exposure to cathode rays. It is decomposed by cold water with the formation of magnesium hydrogen sulphide. In warm water it is said to form polysulphides, and on boiling, hydrogen sulphide is evolved leaving only hydrated magnesia.

Magnesium sulphite $MgSO_3$. When water containing magnesium hydroxide in suspension is saturated with sulphur dioxide, the solution concentrated *in vacuô* at a temperature below 100° and then allowed to cool, rhombohedral crystals of $MgSO_3,6H_2O$ are deposited (Hartog, Compt. rend. 104, 1793).

A basic magnesium sulphite of the composition $MgSO_3{\cdot}2Mg(OH)_2$, similarly prepared by passing sulphur dioxide into water holding magnesia in suspension, is used in sugar factories (Bergreen and Licht, Bied. Centr. 1884, 201). The bisulphite is prepared by passing sulphur dioxide into a solution of the sulphite or by the action of sulphurous acid solution on magnesite. Solution of the bisulphite mixed with sulphide are used for extracting cellulose from material containing lignin and pectic substances. Magnesium bisulphite is said to have more solvent action on the free resins of wood than lime. It is more stable than calcium bisulphite and dissolves the non-cellulose matter more completely.

Magnesium sulphate (*Epsom salts*) $MgSO_4$ occurs in the mineral *kieserite* $MgSO_4,H_2O$, in the Stassfurt salt beds; and as *epsomite*

$MgSO_4,7H_2O$

in the gypsum quarries of Montmartre, in Spain, Chile, and in the Mammoth Cave, Kentucky. Kieserite is occasionally found in rhombic prisms, but more generally occurs in granular masses. Epsomite is found both in the massive state and in silky fibrous crystals. Natural crystals of epsomite more than a centimetre long have also been found coating the walls of a gypsum quarry in the Department of Hérault, France. The sulphate was in a constant state of exudation, and as it solidified formed a lustrous coating of crystals upon the surface of the gypsum (De Rouville, Compt. rend. 87, 703).

Magnesium sulphate forms the purgative principle of bitter spring waters (hence its name of Bitter salt) such as those of Bath, and Seidlitz, Saidschutz, and Pullna in Bohemia. At the three latter places it is obtained by digging pits into which the bitter water runs, and allowing the solution thus collected to evaporate in shallow pans.

The magnesium sulphate of commerce is now chiefly obtained from the kieserite of Stassfurt.

The crude kieserite obtained from the upper layers (Abraumsalz) of the Stassfurt beds is first freed from magnesium and sodium chlorides by being placed in large sieves, standing in tanks of water. The two salts mentioned dissolve out, whilst the kieserite, which is very sparingly soluble in water, falls through the meshes of the sieves in a state of fine powder. Any gangue or other impurities such as anhydrite or larger lumps of rock salt remain behind in the sieves. The kieserite powder is then packed into conical wooden moulds, where it sets to a compact solid, owing to its combining with six more molecules of water to form epsomite. This solid 'stone' is then dried and afterwards powdered. In this condition it contains from 80 to 90 p.c. of $MgSO_4$ and about 1 to 2 p.c. of sodium chloride. A large quantity is brought into the market in this form. The rest is crystallised from water and brought into commerce as Epsom salts

Another mode of manufacturing magnesium sulphate, which was almost universally employed before the working of the Stassfurt beds, consists in decomposing dolomite, magnesium limestone $(CaMg)CO_3$, with oil of vitriol. As calcium sulphate is only sparingly, while magnesium sulphate is readily soluble, the separation offers no difficulty.

The dolomite is first calcined, when on treating the hot mass with a small quantity of water it is readily broken up into powder. This powder is then suspended in water in large digesters constructed of wood lined inside with lead and Yorkshire flags. For a digester 6 feet square and 7 feet deep, about 3 tons of dolomite would form a convenient charge. Into this emulsion are then poured the contents of twelve carboys of sulphuric acid, and water added until the sp.gr. becomes 1·125 to 1·150. At the end of an hour, when the contents begin to cool down, steam is injected by a leaden pipe which completes the action. Excess of acid must be carefully avoided, as it causes loss in crystallising. The liquor is then run off into a settler made of lead or flags, but not of iron; after settling the clear solution is siphoned over into an iron evaporating pan, where it is evaporated down to 66° of Twaddell's hydrometer. The clear concentrated liquor stands for an hour or two to allow any suspended matter to settle, after which it is conveyed to the coolers, which are made of wood, flags, or, best of all, slate, where it is agitated so as to cause the salt to fall in small crystals. The crystals are then drained and finally dried on shelves in a stove room at a temperature not exceeding 80°F.

Magnesium sulphate is largely used in the Lancashire cotton trade in the process of warp-sizing; it is also employed for medicinal and agricultural purposes and for dyeing with the aniline colours.

The crystals have the composition of epsomite $MgSO_4,7H_2O$, and form right rhombic prisms, resembling those of the sulphates of zinc and nickel. They have a sp.gr. of 1·676 (Thorpe and Watts, Chem. Soc. Trans. 37, 106). On heating, they melt in their water of crystallisation, lose 6 molecules of water at 150° and the seventh at 200°.

A salt also having the composition $MgSO_4,7H_2O$ is occasionally deposited from cold supersaturated solutions in monoclinic prisms isomorphous with those of ferrous sulphate $FeSO_4,7H_2O$. By crystallisation of the ordinary salt above 40° monoclinic prisms of a hydrate $MgSO_4,6H_2O$, of sp.gr 1·734, are obtained. By drying the heptahydrate over oil of vitriol to constant weight, $MgSO_4,5H_2O$, of sp.gr. 1·869 is obtained. A salt of the composition $MgSO_4,2H_2O$, sp gr. 2·373, may also be prepared by boiling finely powdered Epsom salts with absolute alcohol The sp.gr. of the monohydrate $MgSO_4,H_2O$ is 2·445 and that of the anhydrous salt 2·709 (Thorpe and Watts, *l.c*).

An octahydrate is capable of existence in solutions containing 32 p.c. of sodium sulphate at 30°, but changes to the heptahydrate if the amount of sodium sulphate exceeds 32 p.c. (Shirô Takegami, J. Chem. Soc. Japan, 1921, 42, 441).

Magnesium sulphate is readily soluble in water. According to Gay-Lussac 100 parts of water dissolve 25·76 parts of the anhydrous salt at 0° and 0·47816 part for every degree beyond. One part of Epsom salts dissolves in 0·79 part of water at 18·75°, forming a liquid of sp.gr. 1·2932.

The table on page 194, due to Schiff (Annalen, 108, 336), shows the amounts of the sulphate in solutions of different specific gravities.

Magnesium sulphate also dissolves in dilute alcohol, but is insoluble in absolute alcohol.

Magnesium hydrogen sulphate $MgH_2(SO_4)_2$. If 2 parts of anhydrous magnesium sulphate are dissolved in 100 parts of boiling sulphuric acid of sp.gr. 1·7 and the solution evaporated at the boiling-point, $MgH_2(SO_4)_2$ is deposited in prisms. On cooling, an acid salt of the composition $MgSO_4·3H_2SO_4$ crystallises out in small shining tables which fuse and decompose when heated.

Magnesium sulphate forms an isomorphous

Sp.gr. at 23°	Per cent. of $MgSO_4,7H_2O$	Per cent. of $MgSO_4$
1·0048	1	0·488
1·0096	2	0·975
1·0193	4	1·951
1·0290	6	2·928
1·0387	8	3·904
1·0487	10	4·878
1·0587	12	5·854
1·0688	14	6·830
1·0790	16	7·806
1·0894	18	8·782
1·0997	20	9·756
1·1[illegible]	22	10·732
1·1209	24	11·708
1·1316	26	12·684
1·1426	28	13·660
1·1536	30	14·634
1·1648	32	15·610
1·1760	34	15·586
1·1875	36	17·562
1·1991	38	18·538
1·2108	40	19·512
1·2228	42	20·488
1·2349	44	21·464
1·2472	46	22·440
1·2596	48	23·416
1·2722	50	24·390
1·2850	52	25·366
1·2980	54	26·341

series of double salts with the sulphates of the alkali metals, of the general formula

$$MgSO_4 \cdot M_2SO_4,6H_2O,$$

which crystallise in monoclinic prisms.

Magnesium potassium sulphate

$$MgK_2(SO_4)_2,6H_2O$$

is found in the Stassfurt salt deposits and is known as *schonite*, also as a volcanic product (*picromerite*). It is prepared by dissolving the salts in molecular proportions and crystallising. It forms monoclinic prisms.

Magnesium ammonium sulphate

$$Mg(NH_4)_2(SO_4)_2,6H_2O$$

is found in the fumeroles of Tuscany and is known as *cerbolite*. Prepared artificially it crystallises in monoclinic prisms and is isomorphous with the potassium double salt.

Magnesium silicide (Compt. rend. 154, 116) is readily prepared in quantity by ramming an intimate mixture of dried quartz powder (200 parts) with magnesium powder (100 parts), igniting with a little magnesium on the surface and covering to exclude air. A bluish-black mass of magnesium silicide is so obtained. Treatment with hydrochloric acid evolves a gas containing 6–7 p.c. of silicon hydrides.

Magnesium silicates occur abundantly in nature and some of them have been prepared artificially. The main features of the binary system $MgO-SiO_2$ as investigated by the American Geo. physic[illegible] School are: magnesia has a melting-point of about 2800°; fosterite crystallises at 1890° and forms a eutectic at 1850° with magnesia. There is no eutectic between fosterite and clino-enstatite, but the latter and cristobalite (m.p. 1625°) form an eutectic at 1543°. The introduction of lime-alumina-silicate into the system not only gives rise to anorthite but magnesium aluminate (spinel) $MgAl_2O_4$ may result. The more important silicates are the following:—

Forsterite Mg_2SiO_4 occurs in crystals in the volcanic ejections of Monte Somma. Ebelmen (Ann. Chim. Phys. [iii.] 33. 58) obtained the mineral artificially by fusing silica and magnesia in proper proportions with boric acid. The crystals obtained were similar to those from Vesuvius. Forsterite forms with the corresponding calcium orthosilicate (*monticellite*) an isodimorphous group of mixed crystals (V. Poschl, Tsch. Min. Mitt. 26. 413).

Olivine $nMg_2SiO_4+Fe_2SiO_4$ is a constituent of many basic rocks. It crystallises in the rhombic system. The olive-green and bottle-green crystals are used as gemstones under the name of peridote. Magnesium silicate forms isomorphous mixtures with iron orthosilicate, but there is a gap in the series (V. Poschl, *loc. cit.*)

Enstatite $MgSiO_3$ the metasilicate, occurs in nature crystallised in the rhombic system. Ebelmen (*loc cit.*) obtained it by fusing magnesia and silica with boric acid in proportions corresponding with the metasilicate; Poschl (*loc. cit.*) has shown that it forms with diopside ($CaMgSi_2O_6$) an isodimorphous series similar to that given by magnesium sulphate and ferrous sulphate.

Sepiolite $2MgO3SiO_2 2H_2O$ is a compact, earthy hydrated silicate, sometimes known as meerschaum.

Talc $H_2Mg_3(SiO_3)_4$ occurs as foliated masses, compact as steatite; the soft variety is known as soapstone or French chalk.

Serpentine $H_4Mg_3Si_2O_4$ forms large rock masses and usually contains ferrous oxide. The fibrous variety is known as *chrysotile* and comes into commerce under the general name of asbestos.

Magnesium titanate $MgTiO_3$ occurs in nature as *geikielite*.

Magnesium citrate $Mg_3(C_6H_5O_7)_2,14H_2O$ is obtained as a crystalline crust when magnesia is dissolved in slightly more than an equivalent quantity of a solution of citric acid, and the solution evaporated at about 50°. It is very soluble in water, and is often preferred to Epsom salts as a mild purgative on account of its pleasanter taste.

The citrate of magnesia of the shops, so popular as an effervescent salt, may be prepared by mixing 16 parts of sodium bicarbonate, 10½ of tartaric acid, 4 of citric acid, about 12 of sugar, ½ part of Epsom salts, and 2 parts of crystallised sodium bisulphate, and heating on an enamelled iron plate until it becomes spongy from the escape of carbon dioxide. The cooled mass is then put through sieves of four to six meshes per square inch. In this granular form it is again heated until quite dry. The solution of the granules in water, after the liberation of the carbon dioxide, contains principally citrate and tartrate of soda and sugar.

It may also be prepared by making a mixture of magnesium citrate, prepared by dissolving magnesia in citric acid solution and crystallising, with sodium bicarbonate, citric acid and sugar, and rendering granular by moistening with alcohol and drying.

The magnesia preparation called *sinodor*, used for removing unpleasant odours and for disinfecting and preserving purposes, is obtained by heating neutral magnesium acetate with magnesium oxide until the mass assumes a pasty consistency. It consists of basic magnesium acetate containing excess of magnesium hydroxide (Kubel, Pat. 18090, Nov. 1881).

Magnesium is usually estimated quantitatively by precipitating an ammoniacal solution with sodium or ammonium phosphate. The precipitate is washed with ammonia water, ignited and weighed as pyrophosphate. This occasionally turns grey on ignition, especially in contact with fibres of filter paper or other form of organic matter. By moistening the ignited mass with a few drops of ammonium nitrate solution and reheating the colour is removed.

Volumetric methods employed for limestones and dolomites depend upon (1) determination of total CaO+MgO by acid and alkali titration less the amount of CaO separately estimated. (2) Solution in standard HCl and titration with NaOH cold for CaO with phenolphthalein as indicator and further titration in boiling solution depending upon the complete precipitation of magnesia hydroxide as indicated by a permanent pink colour. G. S. B.

MAGNESIUM-PERHYDROL. *Biogen.* A combination of hydrogen peroxide (perhydrol) and magnesia and magnesium peroxide. Used as an internal antiseptic.

MAGNETIC IRON ORE *v.* MAGNETITE; IRON.

MAGNETIC PYRITES *v.* PYRRHOTITE.

MAGNETITE, or Magnetic iron ore. A mineral of the spinel group, consisting of magnetic oxide of iron, Fe_3O_4 or $FeO{\cdot}Fe_2O_3$; an important ore of iron (Fe 72·4 p.c.). Sharply developed crystals with bright faces are not uncommon; these belong to the cubic system and usually have the form of the regular octahedron or the rhombic-dodecahedron. Granular to compact masses are, however, more abundant. The colour is iron-black with a dull, sub-metallic lustre and a black streak. Sp.gr. 5·18; hardness 6. The mineral may be always readily recognised by its strong magnetic character: small fragments are picked up by a magnetised knife-blade. Only occasionally are specimens magnetic with polarity (*v.* LOADSTONE) For the magnetic properties of varieties of magnetite, *see* Wilson and Herroun (Proc. Phys. Soc. London, 1919, 31, 299). The titaniferous magnetites, which are also of frequent occurrence, consist of an intimate intergrowth of magnetite with ilmenite or rutile (*v.* J. T. Singewald, The Titaniferous Iron Ores in the United States, their Composition and Economic Value, U.S. Bureau of Mines, 1913, Bull. 64).

As small grains and crystals, magnetite is of wide distribution in many kinds of igneous rocks, especially the darker coloured with a low silica percentage. In such rocks it sometimes forms rich segregations available for mining; as in the Ural Mountains, and at Kirunavara and Gellivara in Swedish Lapland. Other important deposits, *e.g.* some of those in southern Sweden and Norway, have been formed by the metamorphism of pre-existing iron-ores, where these have been subjected to the baking action of intrusive masses of igneous rock. Extensive deposits of magnetite are also mined in the crystalline Archæan rocks of the Adirondack region of New York and in Canada (H. Ries, Economic Geology, New York, 1916).

L. J. S.

MAGNOFERRITE *v.* IRON.

MAHUA or **MAHWA FLOWERS.** The flowers of *Bassia longifolia* and *B. latifolia.* May be used as a source of alcohol. They contain dextrose, levulose, maltose, sucrose, pentoses, the total sugar being greatest when the flowers are ready to fall, when it amounts to 60–70 p.c. The development of the various sugars at different stages of growth has been studied by Fowler and coadjutors (J. Indian Inst. Sci. 1920, 3, 81). Yields of alcohol up to 90 p.c. of the theoretical were obtained by fermentation of a mash of the flowers with cultures of the natural yeast present in the flower with the addition of sulphuric acid and ammonium phosphate. *Cf.* BASSIA *or* MAHWA FLOWERS, Vol. I.

MAILLECHORT *v.* NICKEL

MAIZE. *Zea Mays* (Linn.). **'Indian corn'** or **'mealies.'** This plant was grown by the aborigines of America; it was introduced into Europe in the sixteenth century, and is now extensively grown in almost all countries possessing sufficiently warm climates. It grows to a height of from 5 to 12 or even 15 feet.

Many varieties of maize are known, differing greatly in size, shape, colour, and composition of the grain and in the arrangement of the grain around the cob.

The average composition of all varieties of maize has been given under CEREALS.

South African, American, and Australian grown maizes contain distinctly less moisture than European samples. White and yellow are the commonest colours of the maize grain, but orange, red, blue, violet, and even black grains are known, as well as striped ones.

The separate parts of white American horsetooth maize have been analysed by Plagge and Lebbin in 1897 (quoted by Konig). They obtained the following results:—

	P.c. of whole grain	In the dry matter, p.c.				
		Water	Protein	Fat	Carbohydrates	Ash
Germ .	11·78	6·70	13·75	29·36	46·99	7·23
Husks . .	9·35	8·66	8·32	7·94	82·81	1·63
Horny part of starch	49·79	12·16	8·04	0·64	91·11	0·21
Mealy ,, ,,	29·08	9·68	6·46	0·93	92·97	0·34
Whole grain .		11·38	8·09	5·79	84·61	1·51

Hopkins, Smith and East (J. Amer. Chem. Soc. 1903, 25, 1166) determined the distribution of the proteids in maize grains of (*a*) low (9·89 p.c.), (*b*) medium (11·33 p.c.), and (*c*) high (12·64 p.c.) protein content. Their results were—

	(*a*)	(*b*)	(*c*)
Germ . .	19·31	20·14	18·45
Husks . .	2·75	2·07	1·85
Horny portion .	53·07	59·03	64·88
Mealy portion .	23·98	17·63	14·22
Tip caps . .	0·89	1·14	0·59

They found that the germ contained almost all the oil and about ten times the percentage of ash of the other parts of the grain. Hopkins, indeed (Bull. 55, Illinois Agric. Stat. 1899, 310), finds it possible to classify samples of maize according to their richness in protein or fat by mechanical examination only, the fat being mainly dependent upon the proportion of germ in the grain and the nitrogenous matter being largely determined by the proportion of horny or glutinous matter.

For proteids and oil of maize, *v.* CEREALS.

The injurious effect of a diet consisting largely of maize upon animals has been ascribed to the absence of tryptophan among the products of hydrolysis of *zein*, the characteristic protein of maize (Willcock and Hopkins, J. Phys. Chem. 1906, 35, 88); also to the presence of much phenylalanine and tyrosine among such products, and the ease with which they split off phenolic compounds, thus producing phenolic poisoning (Baglioni, Atti. R. Accad. Lincei. 1908, 17, i. 109).

According to McCallum, Simmonds and Pitz (J. Biol. Chem. 1916, 28, 153) the proteins of maize contain all the amino-acids essential for growth and also the accessory factors 'fat-soluble A' and 'water soluble B,' the former, however, being present in insufficient quantity to allow of maximum growth. The addition of butter effects a marked improvement in the growth of animals whose sole source of protein is maize. The inorganic content of maize is not suitable for the needs of normal growth.

The 'non-nitrogenous extract' of maize consists mainly of starch and cellulose, but includes also cane sugar, dextrin, and gum.

As the average of several determinations of the soluble carbohydrates in various types of maize, Konig gives the following numbers:

Maize from		Number of determinations	In the original substance, p.c. Sugar	Dextrin and gum	Starch, etc
South eastern Europe		8	1·76	2·83	61·20
Italy . . .		22	2·22	1·09	64·41
America	Flint corn	23	2·29	2·30	64·04
	Dent corn	11	2·64	3·62	62·39
	Sweet corn	10	4·64	14·47	43·47

Stone (Bull. 34, O. Exp. St. 14) extracted 0·25 p.c. cane sugar from ordinary and 3·5 p.c. from sweet maize, but could not detect invert sugar in the former. Tollens and Washburn (J. Landw. 1889, 37, 503) found 9 p.c. of glucose and 7·8 p.c. of sucrose and dextrin in sweet maize, but only a trace of glucose and 1·78 p.c. of sucrose and dextrin in ordinary maize. Stone found about 5 p.c., Tollens 7·08 p.c. of pentosans in maize grain.

For ash of maize grain, *v.* CEREALS.

An objection to the use of large quantities of maize as a cattle food is the effect which it has of lowering the melting-point of the fat produced by the animal (*e.g.* bacon in the case of the pig, butter in the case of dairy cows). Maize is too rich in fat and carbohydrates and too poor in ash constituents, especially lime, to form the sole diet of an animal.

Maize cob—the central portion of the ear—consists largely of cellulose and xylan (25 p.c. of the latter). American analyses show it to contain—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
10·7	2·4	0·5	54·9	30·1	1·4

It is sometimes ground along with the grain, and the product, 'corn and cob meal,' is used as a cattle food.

Maize is also employed as a fodder plant, being cut green and either eaten fresh, or, in some cases, made into hay or ensilage. Though immature maize plants contain a cyanogenetic glucoside (Brunnich, Chem. Soc. Trans. 1903, 788), the quantity of hydrocyanic acid present —not exceeding 0·5 grain per 1 lb. of green material—is so small, that there is little or no danger of poisoning the animals fed upon them.

The following table gives the average composition of certain products from maize:

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Green fodder .	79·3	1·8	0·5	12·2	5·0	1·2
Silage . .	79·1	1·7	0·8	11·0	6·0	1·4
Straw . .	15·0	5·0	1·5	34·5	39·2	4·8
Bran . .	12·5	9·9	3·6	61·5	9·5	3·0
Maize germ cake	11·0	21·0	9·0	43·8	9·1	6·1
Corn & cob meal	15·1	8·5	3·5	64·8	6·6	1·5
Gluten meal .	9·6	29·4	6·8	52·4	1·6	0·7

H. I.

MAIZE OIL (Corn oil) is obtained from the germs of the maize plant, *Zea Mais*, L. The germs are recovered, in the process of manufacturing starch, by sifting and winnowing them from the starch granules in which they are imbedded. The oil is therefore a by-product of starch and glucose works using maize (corn) as their raw material.

Formerly maize oil was obtained as a by-product in alcohol distilleries. When the malted and crushed grain was allowed to ferment, the oil was laid bare and rose to the top in the fermentation vats. Before distilling off the alcohol, the oil was ladled off and purified in a crude fashion by washing, filtering, and 'settling.' Since, however, the presence of the germ imparts an unpleasant flavour to the spirit obtained by fermentation, and the oil so recovered was very impure, and had a different character from the oil expressed from the germs, the older process of fermenting the crushed grain has been abandoned. Nowadays, the corn is first malted, beaten up with water to a fine pulp, and the germs are separated from the starch by sieving. At present, maize oil is manufactured on a very large scale from the isolated germs by expression in hydraulic presses. In a dry condition, the germs contain 53 p.c. of oil, and yield in practice about 40 p.c. The whole grain contains about 4 to 5 p.c. of oil.

In the process patented by Leuders and Bauer (U.S. Pat. 1225664 of 1917) maize is steeped in a solution of sulphurous or other acid, and then crushed and separated from the germs. The latter are washed in water containing sufficient alkali to neutralise the acid left from the steeping, and are then dried and the oil expressed.

Maize oil, if properly prepared, is clear in colour, and does not require refining for commercial purposes. If, however, the oil is badly prepared and allowed to stand in contact with albuminoid matter, it undergoes a process of fermentation, whereby considerable quantities of free fatty acids are produced, and acquires a dark colour which renders it unsuitable for light-coloured soaps. Such oil is therefore bleached in soap works in the same manner as linseed oil.

By distilling the freshly expressed oil with steam for several hours lower esters are dissociated, and the residual oil, when washed and dried, is lighter in colour and less acid, and is more suitable for food.

The freshly prepared maize oil is of a pale yellow or golden-yellow colour, and has a distinctive odour; its taste is pleasant at first, and is most characteristic in that it resembles that of newly ground corn-meal. It is therefore possible to identify the oil by its taste alone.

Maize oil is characterised by its high amount of unsaponifiable matter, amounting to as much as 1·55 and even 2·32 p.c. The unsaponifiable matter consists of lecithin, and of an alcohol which appears to be identical with sitosterol (phytosterol). The sp.gr. of maize oil is 0·9215 to 0·927 at 15·5°. The saponification value is 190 to 192, and the iodine value varies between 120 and 130.

The saturated fatty acids in maize oil amount to about 5 p.c. and appear to consist of palmitic, stearic, and arachidic acids. As to liquid fatty acids, linolenic acid is absent, but the oil contains considerable amounts of linolic acid in addition to oleic acid. Baugham and Jameson (J. Amer. Chem. Soc., 1921, 43, 2696) found maize oil to consist of glycerides of the following fatty acids: oleic, 45·4; linolic, 40·9; palmitic, 7·7; stearic, 3·5, arachidic, 0·4, and lignoceric, 0·2 p.c. No hypogæic acid was present. The oil has somewhat better drying powers than cotton-seed oil, but differs from the latter in that it is not oxidised with equal energy when finely subdivided on cotton waste.

Well-refined maize oil is used for edible purposes ('salad oil'). Since its 'grainy' taste is objectionable, the edible quality is frequently a mixture of maize oil with edible cotton oil and other edible oils. Maize oil is also used in the manufacture of margarine ('oleomargarine' of the United States), as also in the manufacture of compound lard (replacing cotton seed oil). Such maize oil as cannot be employed for edible purposes is used chiefly in the manufacture of soft soap, for which it is eminently suitable. A cotton 'softener' largely used in the United States contains maize oil soft soap. Maize oil is not suitable for hard soaps of acceptable quality.

J. L.

MALACHITE. An ore of copper, crystallising in the monoclinic system, but usually occurring as mamillated and botryoidal forms, or as fibrous, compact, or earthy masses of a bright green colour. It is a basic copper carbonate $H_2Cu_2CO_5$ (or $CuCO_3+CuO_2H_2$), having a sp.gr. of 3·9 to 4·0, and hardness 3½ to 4. Heated in a tube, it evolves water and turns black, while on charcoal it yields metallic copper. Malachite is frequently found as an alteration-product of other copper ores, and occurs as a pseudomorph after cuprite, &c. If derived from copper pyrites it is generally accompanied by limonite. Malachite is not only important as an ore of copper (Cu, 57·4 p.c.), but is valued as an ornamental stone, since it takes a good polish and is prettily marked with light and dark green bands of colour. It is chiefly used for vases and small boxes, but its comparative softness stands in the way of its extensive use in jewellery. Large slabs are not generally attainable, but small pieces are skilfully joined together, the interstices being filled in with powdered malachite, and the whole polished; in this way it becomes easy to employ it for inlaid and encrusted furniture, especially for table-tops of considerable size. Malachite is also used to a limited extent as a green pigment, but the term 'malachite green' has been extended to certain organic dyestuffs. Malachite is widely distributed as a mineral, being found in greater or less quantity in most copper deposits, but the finest examples occur near Nizhni-Tagilsk and Gumeshevsk in the Ural Mountains, at Burra-Burra and Wallaroo in South Australia, Namaqualand in South Africa, and Bwana Mkubwa in Northern Rhodesia.

L. J. S.

MALACHITE GREEN, VICTORIA GREEN, BENZAL GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

MALACON. One of the several names that have at different times been applied to altered and hydrated forms of zircon (*q.v.*). This name (from *μαλακός*, soft) was originally given by T. Scheerer, in 1844, to bluish-white tetragonal crystals occurring in granite-pegmatite at Hittero in Norway, which differed from the accompanying zircon in containing 3 p.c. of water, and in their lower degree of hardness (H. about 6, instead of 7½ as for zircon). The material is optically isotropic, has sp.gr. about 3·9, and is often somewhat radioactive. When heated, it suddenly glows brightly, and gives off water and gas; it then has the properties of ordinary zircon. The gas given off consists largely of carbon dioxide, together with some hydrogen, nitrogen, helium, and argon (C. F. Hogley, Phil. Mag. 1909, 18, 672). Similar altered zircon, referred to 'malacon,' has been described from Chanteloube in France, the Ilmen Mountains in the Urals, and several other localities. That from Madagascar contains 9·5 p.c. water (A. Lacroix, Minéralogie de Madagascar, 1922, 239).

L. J. S.

MALAKIN *v.* SYNTHETIC DRUGS.

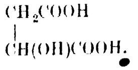
MALARIN. Trade name for the citrate of acetophenone-phenetidide, prepared by heating equivalent proportions of acetophenone and *p*-phenetidine either alone or with addition of dehydrating agents. Crystallises in yellow needles, m.p. 88°, readily soluble in hot alcohol, ether, or glacial acetic acid.

MALAYAN CAMPHOR *v.* CAMPHORS.

MALE FERN *v.* FILIX-MAS.

MALEIC ACID *v.* FUMARIC ACID.

MALIC ACID, *Hydroxysuccinic acid* (*Acide malique*, Fr.; *Aepfel saure*, Ger.)



$$\begin{array}{l} CH_2COOH \\ | \\ CH(OH)COOH. \end{array}$$

This acid contains an asymmetric carbon atom and hence can occur in three modifications, viz. a dextrorotatory form, a lævo-rotatory form, and an inactive variety. The lævo-rotatory variety occurs free or in the form of salts in many plant juices and hence is frequently termed *ordinary* malic acid. *l*-Malic acid was discovered by Scheele in 1785 in sour apples, and Liebig in 1832 ascertained its composition. The inactive acid was first obtained by Pasteur in 1852 from inactive aspartic acid, and by Kekulé in 1861 from bromosuccinic acid. The *d*-acid was firs obtained by Bremer in the reduction of *d*-**tartaric acid.**

Preparation.—l-Malic acid occurs free in unripe grapes (Ordonneau, Bull. Soc. chim. 1891, 261); in apples, gooseberries, strawberries, cherries, tomatoes (Albahary, Compt. rend 145, 131), mountain ash berries (*Pyrus Aucuparia*) (Liebig, Ann. 5. 141); in the berries of *Hippophaë rhamnoides* (Erdmann, Ber. 1899, 3351); and of *Berberis vulgaris*; in honey (Hilger, Zeitsch. Nahr. Genussm. 8, 110, Farnsteiner, *ibid.* 1908, 598): in fruit juices (Kunz and Adam, Chem. Zentr. 1906, i. 1849); in ferns (Regnault, Ann. Chim. Phys. 1836, 208); in tamarind (Adam, Chem. Zentr. 1905, ii. 1042); in baobab fruits (Franck and Marckwald, Chem. Zeit. 1911, 587), &c. Sumt contains potassium malate to the extent of 2½ p.c. of the solid residue and it is a product of excretion (A and P. Buisine, Compt. rend. 106, 1426); *l*-malic acid is also found in the calcium precipitate formed in the treatment of beetroot (Lippmann, Ber. 1891, 3299). It can be prepared from the unripe berries of *Pyrus Aucuparia* (Ehrh.) (Hagen, Annalen, 38, 257), or of *Berberis vulgaris* (Linn.) (Lennsen, Ber. 1870, 966) in the following manner The expressed juice is evaporated, filtered, heated to boiling, and saturated with milk of lime. The calcium malate which separates is dissolved in hot dilute nitric acid (1 : 10); on cooling, the solution deposits the acid malate, which is purified by recrystallisation from water. In order to obtain malic acid from it, its solution is precipitated with lead acetate and the lead salt is decomposed with sulphuretted hydrogen (Brœksmit, Pharm. Weekbad. 42, 637) The precipitate known as 'sand' which is formed during the evaporation of maple sap contains 60-80 p.c. of calcium malate and constitutes a readily available source of malic acid. The annual production of 'sand' in America and Canada is estimated to be 100–330 tons, corresponding to 50-165 tons of calcium malate. Malic acid may be obtained from the juice of cherries or grapes by means of the cinchonine salt, which is very insoluble, the cinchonine salts of the other acids remaining in solution (Lindet, Bull. Soc. chim. 1896, 15, 1160). Castoro recommends separating malic acid from the expressed juice of the rhubarb, in which it occurs as the acid potassium salt, by means of its strontium salt (Chem. Soc. Abstr. 1902, i. 259). Sahasrabuddhe (Agric. Rep. Inst. Pusa, 1914) describes its preparation from *Cicer arietinum*; the acid secretion of this plant contains 19 parts of malic to 1 part oxalic acid, it is washed off the plant every 6 days, and furnishes considerable quantities of malic acid.

l-Malic acid can be obtained from *l*-chloro- or *l*-bromosuccinic acid through the action of moist silver oxide, mercuric oxide, &c., or from *d*-chloro- or *d*-bromosuccinic acid by the action of potassium hydroxide, or hydroxides of the other alkali metals (Walden, Ber. 1896, 135; 1897, 2795, 3148; 1899, 1833, 1853). It can also be obtained by the action of nitrous acid on *l*-asparagine or *l*-aspartic acid (Walden, *l.c.*); and by the action of *Bac. aerogenes* on succinic acid (Ber. 1899, 1915). By heating the ammonium salt of inactive malic acid to 80°, the active salt crystallises out from the solution of the inactive salt (Kenrick, Ber. 1897, 1749; Van 't Hoff and Dawson, *ibid.* 1898, 528).

d-Malic acid occurs naturally in *Crassulaceæ* (Aberson, Ber. 1898, 1432; Walden, *ibid.* 1899, 2706). It can be obtained synthetically by methods similar to those for obtaining *l*-malic acid (Walden, *l.c.*; Piutti, Ber. 1886, 1693; Bremer, *l.c.*). Racemic acid can be reduced to inactive malic acid, which can be resolved into *d*- and *l*-malic acids by cinchonine (Bremer, Ber. 1880, 351; Rec trav. chim. 4, 180).

Inactive malic acid can be prepared by methods similar to those above (Tanatar, J. Russ. Phys. Chem. Soc. 1891, i. 339; Annalen, 273, 37; Van 't Hoff, Ber. 1885, 2170, 2173). It is also obtained by heating fumaric or maleic acids with caustic soda to 100° (Van't Hoff, *l.c.*; Lloyd, Annalen, 192, 80; Bremer, *l.c.*; Skraup, Monatsh. 12, 113); by heating chloral and malonic acid with acetic acid and treating the γ-trichloro-β-hydroxybutyric acid thus formed with potassium hydroxide (Garzarolli-Thurnbackh. Monatsh. 12, 556); and by reducing oxalacetic acid with sodium amalgam in acid solution (Wislicenus, Ber. 1891, 3416; 1892, 2448).

Properties.—Inactive malic acid. Melts at 130°-131°; sp.gr. 20°/4° 1·611. Affinity constant (Walden, Ber. 1896, 1698). The diethyl ester is obtained by reducing ethyloxalacetate with aluminium amalgam (Wislicenus, J. pr. Chem. 1896, [ii] 59, 18) Dielectric constant *v.* Drude, Zeitsch. physikal. Chem. 23, 310).

d-Malic acid. Physical properties, *v. l-malic acid.*

l-Malic acid. Crystallises in colourless needles, m.p. 100°. Very soluble in water or alcohol. Rotation of acid (*v.* Nasini and Gennari, Gazz. chim. ital. 25, i. 422; Zeitsch. physikal. Chem. 1896, 19, 113; Winther, Chem. Zentr. 1896, ii. 22; Woringer, Zeitsch. physikal. Chem. 1901, 36, 336; Stubbs, Trans. Chem. Soc. 1911, 2265). Thermal constants, *v.* Massol. Compt. rend. 113, 800. Dissociation constants, *v.* Smith and Jones, Amer. Chem. J. 50, 1. The esters are prepared by adding dry silver malate in small quantities at a time to an excess of alkyl iodide and completing the reaction by heating on the water-bath; or by treating malic acid and an alcohol with hydrochloric acid or sulphuric acid. When the former method is used, a small quantity of a more active substance is always present, *e.g.* in the preparation of ethyl malate, ethyl ethoxysuccinate is also produced (Purdie and Lander, Chem. Soc. Trans. 1898, 293; Purdie and Pitkeathly, *ibid.* 1899, 154). The dimethyl ester boils at 129° (16 mm.) and has sp.gr. 1·2301 at 20°/4°; the diethyl ester boils at 138° (25 mm.) and has sp.gr. 1·1340 at 20/4° (Purdie, *l.c.*; Walden, Zeitsch. physikal. Chem. 1895, 17, 245; Frankland and Wharton, Chem. Soc. Trans. 1899, 338). Rotation, *v.* also Anschutz and Reitter, Zeitsch, physikal. Chem. 1895, 16, 493; Clough Trans. Chem. Soc. 1915, 96. Dielectric constant, v. Walden, *ibid.* 46, 103. According to H. Traube (Zeitsch. Kryst. Min. 1899, 31, 160), the best method for the preparation of the salts of malic acid is by the interaction of strontium hydrogen malate with the sulphate of the metal. A detailed account of the composition and crystallographic properties of the salts is given.

On heating malic acid to 100° for 24 hours, there results malomalic acid $C_5H_7O_3(CO_2H)_3$, and on heating *in vacuô* at 180° there is formed an anhydride, *malide* $C_8H_8O_8$ and small quantities of fumaric acid and maleic anhydride (Walden, Ber. 1899, 2716). Prolonged heating at 140°–150° yields fumaric acid as the main product, and at 180°, fumaric acid, maleic anhydride, and water are formed. Oxidation with hydrogen peroxide in the presence of a ferrous salt yields oxalacetic acid (Fenton and Jones, Chem. Soc. Trans. 1900, 77); with hydrogen peroxide in a sealed tube at 120°, tartaric acid (Zinno, Mon. Scient. 16, ii. 493); with potassium permanganate, oxalacetic acid (Denigès, Compt rend. 130, 32); with nitric acid, oxalic acid; with potassium dichromate, malonic acid. Reduction with hydriodic acid yields succinic acid. By heating malic acid with sulphuric acid, the half aldehydes of malonic acid and formic acid are produced, the former of which is changed into coumalic and trimesic acids (Von Pechmann, Annalen, 264, 261): heating with glycerol gives rise to carbon dioxide and acrolein (de Coninck and Raynaud, Compt. rend. 135, 1351). Heating with excess of alcoholic potash results in racemisation (McKenzie and Thompson, Trans. Chem. Soc. 1905, 1004). Carbon dioxide, acetaldehyde, and crotonic aldehyde are formed by the electrolysis of a concentrated aqueous solution of the sodium salt (Miller and Hafer, Ber. 1891, 170). The coumarins are produced when malic acid is heated with phenols and sulphuric acid (Pechmann, Ber. 1884, 929, 1646). Benzaldehyde and malic acid in piperidine at 150°–160° react to form β-benzoyl propionic acid (Mayrhofer and Nemeth, Monatsh. 1903, 24, 80). Heated with hydrobromic acid, malic acid yields bromosuccinic acid and with phosphorus pentachloride chlorosuccinic acid. A concentrated solution of an alkaline malate gives with calcium chloride on boiling a precipitate of calcium malate. Ammonium salts prevent the precipitation; addition of alcohol aids it. Piñuera (Compt. rend. 1897, 124, 291) uses as a reagent a solution containing 0·02 gram β-naphthol per c.c. strong sulphuric acid. If 0·05 gram of dry substance is added to 15 drops of the reagent in a porcelain dish and malic acid is present, a yellow-green coloration is produced, changing to light yellow on heating and orange on dilution. De Coninck (Bull. Soc. chim. 1914, 93) states that a red colour is given on adding calcium salicylate, less stable than that produced by succinic acid. Details as to estimation *v.* Clowes, J. Amer. Chem. Soc. 1908, 30, 1285; Pozzio-Escot, Bull. Soc. chim. Belg. 1908, 22, 413. Photo-chemical decomposition of solutions of malic acid gives formaldehyde, acetaldehyde and formic, acetic, glycollic, and oxalic acids (Spoehr, Biochem. Zeitsch. 57, 95).

Malic acid is present in wines (Mayer, Zeitsch. öffentl. Chem. 1909, 15). When fermentation is carried out with pure yeast on sterile musts, no decomposition of malic acid occurs until the wines become contaminated with micro-organisms in the ordinary cellar operations. Then gradual fermentation sets in and this liberates the carbon dioxide necessary to prevent premature decay (Rosenstiehl, Compt. rend. 1908, 147, 150; *cf.* Mestregat, *ibid.* 1907, 145, 260; Emmerling, Ber. 1899, 1915). Lebedew showed, however, that solutions containing 2 p.c. malic acid are fermented by certain yeasts, higher concentrations being more feebly attacked; the products are lactic acid and CO_2 (J. Soc. Chem. Ind. 1917, 300). Seiffert (Chem. Zentr. 1903, ii. 257) has shown that malic acid is gradually converted into lactic acid by an anærobic micrococcus (*Micrococcus malolacticus*); this is also brought about by *Bacillus lactis aërogenes* (Emmerling, *l.c.*) *Bacillus cloacæ* in the presence of oxygen gives acetic, succinic, and carbonic acids (Thompson, Proc. Roy. Soc. B, 84. 500).

Detection and estimation in wines and fruit juices, *v.* Schneider (J. Soc. Chem. Ind. 1890, 1068); Micko (Zeitsch. anal. Chem. 31, 465; 32, 481; Chem. News, 68, 286); Hilger (Chem. Zentr. 1900, ii. 597; Zeitsch. Nahr. Genussm. 1903, 6, 721); Kunz (Apoth. Zeit. 1905, 20, 677); Mestrezat (Compt. rend. 1906, 143, 185; Ann. Chim. anal. 1907, 173; 12, 194); Jörgensen (Zeitsch. Nahr. Genussm. 13, 241); Heide and Steiner, *ibid.* 1909, 17, 307); Dutoit and Duboux (Bull. Soc. Chim. [4], 13, 832). *In tobacco*, Kissling (Chem. Zeit. 1898, 22, 1; 1899, 23, 2). *In cider vinegar*, Leach and Lythgoe (J. Amer. Chem. Soc. 1904, 25, 375).

Ammonium malate is prepared by leading dry NH_3 into an ethereal solution of the acid (McMaster, Amer. Chem. J. 49, 294).

Copper malate $C_4H_4O_5Cu$ hard rhombic crystals insoluble in water. A soluble cuprimalate is also described (Pickering, Trans. Chem. Soc. 1913, 1354).

For malates of heavy metals *v.* Pickering Trans. Chem. Soc. 1916, 235.

iso*Malic acid.* Methyltartronic acid, *v.* TARTRONIC ACID.

β-iso*Malic acid.* *β-Hydroxy*iso*succinic acid* $CH_2(OH)CH(CO_2H)_2$. The ethyl ester is obtained by treating formaldehyde with hydrogen chloride and adding to the solution ethylsodiomalonate; the product is hydrolysed with potash and the acid so obtained is a syrup decomposing into acrylic acid on heating (Coops, Rec. trav. chim. 1901, 20, 430; Chem. Weekbad. 1, 535; *cf.* Tanatar, Annalen, 273, 44).

Citramalic acid. *a-Methylmalic acid*

$$CO_2H{\cdot}CH_2(CH_3)C(OH)CO_2H$$

Prepared from acetoacetic ester by means of hydrocyanic acid and hydrochloric acid (Michael, J. pr. Chem. [ii.] 46, 287; Demarcy, Bull. Soc. chim. [ii.] 27, 120; Morris, Chem. Soc. Trans. 1880, 6); by the reduction of chlorocitramalic acid, which is formed from citraconic acid (Carius, Annalen, 129, 160; Morawski, J. 1878, 721); by the action of N_2O_3 on methylaspartic acid (Piutti, Ber. 1893, 2046); by the action of caustic soda on β-bromopyrotartaric acid (Ssemenoff, J. Russ. Phys. Chem. Soc. 31, 289). Melts at 115°–117° and on heating to 200° decomposes into water and citraconic anhydride (Wislicenus, Ber. 1892, 196).

β-Methylmalic acid

$$CO_2H{\cdot}CH(OH){\cdot}CH(CH_3)CO_2H$$

Prepared by heating the ester of methyloxalacetic acid with sodium amalgam in aqueous solution (Wislicenus, Ber. 1892, 199). Colourless syrup.

MALLEABLE CAST IRON *v.* IRON

MALLEBREIN. Trade name for aluminium chlorate.

MALLET BARK. The bark of *Eucalyptus occidentalis* (Endl.), found in Queensland. Employed in tanning; contains from 30 to 50 p.c. of tanning substance. The commercial extract has a density of 22°–24° B. and contains 30–36 p.c. of tanning substance.

MALLOTOXIN *v.* Resins.

MALONAL, MALOUREA. Syns for Veronal (*q.v.*).

MALONIC ACID $CH_2(COOH)_2$, the second member of the oxalic acid series, was first prepared by Dessaignes by oxidising malic acid with potassium dichromate (Annalen, 1858, 107, 251), and was found by Lippmann among the calcium salts formed in beet sugar manufacture (Ber. 1881, 14, 1183). Calcium malonate has been found in a fermented solution of sucrose containing lime-water (von Lippmann, Ber. 1920, 53 [B] 2069). Malonic acid can be obtained by oxidising crude sarcolactic acid with potassium dichromate (Dossios, Zeitsch Chem. 1866, 449); or allylene or propylene with potassium permanganate (Berthelot, Annalen (Supl.) 1867, 5, 97), by the action of fuming nitric acid on hexabromomethylethyl ketone (Demole, Ber. 1878, 11, 1714); or of boiling baryta water on ethyl chloroacrylate (Pinner, *ibid.* 1875, 8, 963); or of silver oxide at 125° on ethyl dichloroacrylate (Wallach, Annalen, 1878, 193, 25): by boiling bromomucic acid with baryta water (Jackson and Hill, Ber. 1878, 11, 289); or by boiling barbituric acid with alkali (Baeyer, Annalen, 1864, 130, 143). Malonic acid is best prepared by the hydrolysis of cyanacetic acid (Conrad, Ber. 1879, 12, 749; Bourgoin, Compt. rend. 1880. 90, 1289). Endemann (D. R. P. 183328, 1907) has devised a method for preparing malonic acid from abietic acid and the accompanying resins, by hydrolysing the resin or abietic acid with sodium hydroxide, oxidising the product with permanganate at 0°, and separating the malonic acid from the mixture of acids by means of its sparingly soluble calcium salt. Malonic acid also occurs among the decomposition products obtained by hydrolysing cellulose nitrate with concentrated alkali solution (Berl and Fodor, Chem. Zentr. 1911, ii. 1039).

Properties and reactions. Malonic acid crystallises in large triclinic plates, m.p 133°–134°, decomposing at a higher temperature into carbon dioxide and acetic acid (for its rate of decomposition, *see* Hinshelwood, Chem Soc. Trans. 1920, 117, 156); when heated under a pressure of 8–10 mm. it sublimes unchanged (Krafft and Noerdlinger, Ber. 1889, 22, 816). For its solubility in alcohol and in ether *v.* Lamouroux, Compt. rend. 1899, 128, 999; Klobbie, Zeitsch physikal Chem 1897, 24, 615.

Malonic acid dissolves in hot acetic anhydride to give a yellowish-red solution with a strong yellowish-green fluorescence, intensified by the addition of glacial acetic acid: the reaction is sensitive, being produced by a milligram of the acid (Kleemann, Ber. 1886, 19, 2030). For its absorption of ultra-violet light *v.* Bielecki and Henri (Ber. 1913, 46, 2596).

When malonic acid or its sodium salt is administered internally it passes only in small quantity into the urine, and leads to an increase of urinary carbonates and to the formation of barbituric acid (Marjori, Chem. Zentr. 1896), ii. 106).

Detection and Estimation.—Malonic acid, or its esters, mixed with anhydrous methyl or ethyl alcohol, containing hydrogen chloride, heated for a few minutes and then neutralised yields on addition of an alcoholic solution of bromomethyl furfuraldehyde and rendering slightly alkaline with alcoholic potassium hydroxide an intense blue fluorescence, Fenton (Pro. Camb Phil. Soc. 1914, 17, 477). Bougault (J. Pharm. Chem. 1913, [vii.] 8, 289) suggests the formation of cinnamylidene malonic acid as a means for detecting malonic acid. Malonic acid or its salts may be estimated by oxidation with permanganate at 80°–90° first in acid and then in alkaline solution, and titrating the excess of permanganate (Durand, Ann. Chim. anal 1903, 8, 330; Cameron and McEwan, Chem Soc. Proc. 1910, 26, 144).

The malonic acid contained in maple products is estimated by precipitation with normal lead acetate and converting the washed precipitate into lead sulphate by evaporation with nitric and sulphuric acids (Albert P. Sy, Chem. Zentr. 1906, ii. 714)

Salts. Malonic acid is a strong dibasic acid forming both acid and normal salts, and the following salts are described: ammonium, barium, cadmium, calcium, cerium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, nickel, potassium, silver, sodium, strontium, uranium, zinc, brucine, pyridine [Massol, Ann Chim. Phys 1894, [vii.], 1, 184; Finkelstein, Annalen, 133, 338; Miczynski, Monatsh. 7, 260; Rimbach, Kilian, Annalen, 1909, 368, 110; Howe, J. Amer. Chem. Soc. 1903, 25, 444; Werner, Chem. Soc. Trans. 1904, 144; Lord, J. Phys. Chem. 1907, 11, 173; Motooki Malsui, J. Coll. Sci. Tōkyō, 1908, 25, ii. 1; Heintzel, Annalen, 149, 129; Mulder, Bull Soc. chim. [ii.] 29, 532; Fay, Amer. Chem. J. 18, 281; Hilditch, Chem Soc. Trans. 1909, 1580; Keiser and McMaster (Amer Chem. J. 1913, 49, 84; Flack, Zeitsch anorg. Chem. 1913, 82, 173; Mazzucchelli and d'Alceo, Atti. R. Accad. Lincei, 1912, [v.] 21, ii, 620; Traube and Goodson, Ber. 1916, 49, 1679; Werner, Annalen, 1911, 386, 1; Pfeiffer, Ber. 1914, 47, 1580).

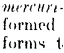
For toluidine hydrogen malonates, *see* Grünwald (J. pr. Chem. 1913, [ii.] 88, 176).

For the absorption spectra of salts of malonic acid *v.* Wright (Chem. Soc. Trans. 1913, 103, 528).

For the dissociation constant of the neutral sodium salt *v.* Datta and Dhar, Chem. Soc. Trans. 1915, 107, 826).

Esters. The *ethyl ester* $CH_2(CO_2Et)_2$, can be prepared from malonic acid by the ordinary processes of esterification (Finkelstein, Annalen, 1864, 133, 338; Conrad, Ber. 1879, 12, 749; Phelps and Tillotson, Amer. J. Sci. 1908, [iv.] 26, 243); but it is more usually prepared by heating cyanoacetic acid with absolute alcohol in the presence of sulphuric acid or in a current of hydrogen chloride (Venable and Claisen, Annalen, 1883, 218, 131; Noyes, J. Amer. Chem. Soc. 1896, 18, 1105; Phelps and Tillotson, *l.c.*), and commonly contains small quantities of ethyl cyanoacetate (Crossley and Gilling, Chem. Soc. Trans. 1909, 95, 27 *f.n.*).

Diethyl malonate is a colourless liquid, b.p. 197·7°–198·2° (corr.), sp.gr. 1·06104 at 15°, 1·05284 at 25° (Perkin, *ibid.* 1884, 45, 508), 1·07607 at 0° (Wiens, Annalen, 1889, 253, 298); m.p. −49·8° (von Schneider, Zeitsch. physikal. Chem. 22, 233. *Diethyl malonate tin tetrachloride* $\mathrm{CH_2(CO_2Et)_2,SnCl_4}$ has m.p. 115°–117°, Pfeiffer and Halperin (Zeitsch. anorg. Chem. 1914, 87, 335). For derivatives of iodo- and bronoanils of the type $\mathrm{C_6X_2[CH(COOEt)_2]_2O_2}$ (where X is Br or I) and their reduction products and bromine derivatives, *see* Jackson and Bolton (J. Amer. Chem. Soc. 1914, 36, 1481). The viscosity of the ester and its relationship to other physical properties are described by Hilditch and Dunstan (Zeitsch. Elektro Chem. 1912, 18, 881), and the desmotropy by Meyer (Ber. 1912, 45, 2864). *Ethyl hydrogen malonate* $\mathrm{HO_2C{\cdot}CH_2{\cdot}CO_2Et}$ (Hoff, Ber. 1874, 7, 1572), has sp.gr. 1·201 at 0° n_D 1·337 at 22° (Massol, Ann. Chim. Phys. 1894, [vii.] 1, 184); b.p. 117°/21 mm., sp.gr. 1·1759 at 19°/19°, n_D 1·4275 at 19° (Marguery, Bull. Soc. chim. 1905, [iii.] 33, 541). *Dimethyl malonate* $\mathrm{CH_2(CO_2Me)_2}$, a colourless liquid, b.p. 181·5° (corr.), sp.gr. 1·16028 at 15°; 1·15110 at 25° (Perkin, Chem. Soc. Trans. 1884, 45, 509); b.p. 180·7° (corr.), sp.gr. 1·1753 at 0° (Wiens, Annalen, 1889, 253, 297); solidifies to a vitreous mass at −80° (von Schneider, Zeitsch. physikal. Chem. 22, 233). Mercuri salts of possible therapeutic value are obtained by shaking mercuric oxide (1 mol.) and methyl malonate (2⅓ mols.) in water at 37°; when the *mono-mercuri-dimalonic ester* $\mathrm{Hg[CH(CO_2Me)_2]_2}$ thus formed is hydrolysed the acid loses $\mathrm{CO_2}$ and forms the *anhydride* of *oxymercuri-acetic acid*



$$\begin{array}{l}\mathrm{CH_2{\cdot}Hg.}\\ \;|\qquad|\\ \mathrm{CO{-}O}\end{array}$$

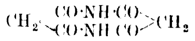
The methyl esters of methyl, ethyl, propyl and allyl malonic acid, or the alkali salts of the acid yield similar compounds (Schoeller and Schrauth, D.R.P. 208634, 1909; 213371, 1909; Bulmann and Hoff, Rec. trav. chim. 1917, 36, 306). *Methyl β-benzoyl-α-phenylethylmalonate* $\mathrm{C_6H_5CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2}$ crystallises in large colourless needles, m.p. 107° (Kohler, Heritage, and McLeod, Amer. Chem. J. 1911, 46, 234). *Ethyl propyl malonate*

$$\mathrm{(CO_2Et)CH_2{\cdot}CO_2Pr}$$

b.p. 211° (corr.), sp.gr. 1·04977 at 0° (Wiens, *l.c.*).—*Dipropyl malonate* $\mathrm{CH_2(CO_2Pr)_2}$, b.p. 228°–229° at 770·3 mm. or 228·3° (corr.); sp.gr. 1·02705 at 0° (Wiens, *l.c.*). *Dibutyl malonate* $\mathrm{CH_2(COOC_4H_9)_2}$, b.p. 251·5° (corr.), sp.gr. 1·0049 at 0° (Wiens, *l.c.*). *Di-l-amyl malonate* $\mathrm{CH_2(COOC_5H_{11})}$, has $[M]_D$ 8·09° (Walden, Chem. Zentr. 1899, i. 327). *Diphenyl malonate* $\mathrm{CH_2(CO_2Ph)_2}$, has m.p. 50°, b.p. 210°/15 mm. *Dibenzyl malonate* $\mathrm{CH_2(CO{\cdot}OCH_2Ph)_2}$, b.p. 234·5°/14 mm. (Bischoff and Hendenström, Ber. 1902, 35, 3452; Auger and Billy, Compt. rend. 1903, 136, 555). *Dimenthyl malonate* $\mathrm{CH_2(CO{\cdot}OC_{10}H_{19})_2}$, m.p. 62°, $[\alpha]_D$ 79·24° (Hilditch, Chem. Soc. Trans. 1909, 95, 1579). *tert-Butyl hydrogen malonate* $\mathrm{CO_2H{\cdot}CH_2{\cdot}CO_2{\cdot}C_4H_9}$ has m.p. 102°–103°, gem.-*Trichloro*-tert-*butyl hydrogen malonate* has m.p. 116° and the *malonate* m.p. 102°–103° (Wolffenstein, Loewy, Bachstez, Ber. 1915, 48, 2035).

Amides and substituted amides. *Ethyl malonamate* $\mathrm{EtO{\cdot}OC{\cdot}CH_2{\cdot}CONH_2}$, m.p. 50°, (Pinner, Ber. 1895, 28, 473); *malonamide* $\mathrm{CH_2(CONH_2)_2}$, m.p. 170°, soluble in 12 parts of water at 8° (Henry, Compt. rend. 1885, 100, 913).

Malonylmalonamide



$$\mathrm{CH_2}\begin{array}{l}\diagup\mathrm{CO{\cdot}NH{\cdot}CO}\diagdown\\ \diagdown\mathrm{CO{\cdot}NH{\cdot}CO}\diagup\end{array}\mathrm{CH_2}$$

m.p. 252°–253°, prepared by condensing malonamide and ethyl malonate, and the alkyl substituted derivatives in which one or more of the methylene hydrogen atoms are replaced by alkyl groups, have no hypnotic properties (Remfry, Chem. Soc. Trans. 1911, 99, 610).

Malondimethylamide $\mathrm{CH_2(CONHMe)_2}$, m.p. 135° (Whiteley, Chem. Soc. Trans. 1903, 83, 24). *Malondiethylamide* $\mathrm{CH_2(CONHEt)_2}$, m.p. 149° (Wallach and Kamenski, Ber. 1881, 14, 170; Backes, West and Whiteley, Chem. Soc. Trans. 1921, 119, 366). *Malondi*-n-*propylamide* $\mathrm{CH_2(CO{\cdot}NHPr^a)_2}$, m.p. 139°; *malondi*-n-butylamide $\mathrm{CH_2(CO{\cdot}NH{\cdot}C_4H_9)_2}$, m.p. 132·5°. *Malondiisobutylamide* $\mathrm{CH_2(CONH{\cdot}C_4H_9)_2}$, m.p. 126°–127°, *malondibenzylamide*

$$\mathrm{CH_2(CO{\cdot}NH{\cdot}CH_2Ph)_2}$$

m.p. 142° (Backes, West and Whiteley, *l.c.*) *Malonanilic acid* $\mathrm{HOOC{\cdot}CH_2{\cdot}CONHPh}$, m.p. 132° with decomposition (Rugheimer, Ber. 1884, 17, 235; Seifert, Ber. 1885, 18, 1358); for its halogen derivatives *see* Chattaway and Clemo (Chem. Soc. Trans. 1916, 109, 101); *methyl malonanilate*, m.p. 42°–43° (Staudinger and Becker, Ber. 1917, 50, 1016); *ethyl malonanilate* m.p. 38°–39° (Rugheimer and Hoffmann, *ibid.* 1884, 17, 739); the p-*iodo derivative* melts at 120° (Chattaway and Constable, Chem. Soc. Trans. 1914, 105, 130); the p-*nitro derivative* melts at 92°–95° (Jacobs and Heidelberger, J. Amer. Chem. Soc. 1917, 39, 1454); *malonmonophenylamide* $\mathrm{PhHN{\cdot}CO{\cdot}CH_2{\cdot}CONH_2,\tfrac{1}{2}H_2O}$ m.p. 153°–154° (Whiteley, Chem. Soc. Proc. 1904, 93); the p-*nitro* derivative melts at 218°–220°, the p-*amino* derivative crystallises with 1 $\mathrm{H_2O}$ and melts at 200°–210° (Jacobs and Heidelberger, *l.c.*); *malonanilide* $\mathrm{CH_2(CONHPh)_2}$, m.p. 225° (Whiteley, Chem. Soc. Trans. 1903, 83, 24); m-*nitromalonanilide*, m.p. (after melting at 173°–177° and resolidifying) 198°–200° (corr.); p-*nitromalonanilide*, m.p. 241°–242°; m-*aminomalonanilide*, m.p. 180°–185° (corr.). (Jacobs and Heidelberger, *l.c.*); *dithiomalonanilide*

$$\mathrm{CH_2(CSNHPh)_2}$$

m.p. 149° (Reissert and Moré, Ber. 1906, 39, 3298). *o-*, *m-* and *p-Malonamidobenzoic acids*

$$\mathrm{CH_2(CONH{\cdot}C_6H_4{\cdot}CO_2H)_2}$$

melt and decompose at 242°, 258°–259° and 270° respectively (von Pollack, Monatsh. 1905, 26, 327); the *ethyl ester* of *p-malonamidobenzoic acid*, $\mathrm{CO_2Et{\cdot}CH_2{\cdot}CONH{\cdot}C_6H_4{\cdot}CO_2H}$, has m.p. 172°–173° (Schiff, Annalen, 1886, 232, 129; Gazz. chim. ital. 1885, 15, 534); *malonyldiphenetidide*

$$\mathrm{CH_2(CONH{\cdot}C_6H_4{\cdot}OEt)_2}$$

has m.p. 226° (Bischoff, Ber. 1898, 31, 3248). The chloro and bromo substituted derivatives of malonanilide and malonanilic acid are described by Chattaway and Mason (Chem. Soc. Trans. 1910, 97, 340). Certain of the salts and ethyl esters of the three isomeric *malontoluidic* *acids* $CO_2H\cdot CH_2\cdot CONHC_7H_7$, were prepared by Rügheimer and Hoffmann (Ber. 1885, 18, 2971). The *o*-, *m*- and *p*- acids melt at 138°–143°, 99°–101°, and 156° respectively; compare also Chattaway and Olmsted (*l.c* 938). *Malondi*-p-*tolylamide* $CH_2(CONH\cdot C_7H_7)_2$, has m.p. 250° *malonmono*-p-*tolylamide* has m.p. 144°; *malondi*-o-*tolylamide* has m.p. 193° (Whiteley, *l.c.*); *dithiomalondi*-o-*toluidide* $CH_2(CSNHC_7H_7)_2$, and the corresponding *p*- isomeride melt at 122°–123° and 145° respectively (Reissert and Moré, Ber. 1906, 39, 3298). *Malondi-α-naphthylamide* $CH_2(CONH\cdot C_{10}H_7)_2$, melts at 225°; the *β*-isomeride melts at 235° (Whiteley, *l c.*) *α-Malonnaphthil* $C_{10}H_7N<\substack{CO\\CO}>CH_2$, has m.p. above 300° (Meyer, Annalen, 1906, 347, 17) *Malondimethylanilide* $CH_2(CONMePh)_2$, m.p. 109° (Freund, Ber. 1884, 17, 133); *malontetraphenylamide* $CH_2(CO\cdot NPh_2)_2$, m.p. 219°–220° with decomposition; *malonmonomethylanilide*

$$NHPhCO\cdot CH_2\cdot CONMePh$$

m.p. 112° (Whiteley, Chem. Soc. Proc. 1904, 93). *Malonylmonobenzanilide* $C_{16}H_{13}O_4N$, m.p. 100°–101° (with decomp.) (Mumm, Hesse and Volquartz, Ber. 1915, 48, 379).

Malonyldiurethane $CH_2(CONH\cdot CO_2Et)_2$, m.p. 124° (Conrad and Schulze, Ber 1909, 42, 729). *Malonylpiperidide* $C_{13}H_{22}O_2N_2$, m.p. 57° (Franchimont, van Rijn and Friedmann, Rec. trav. chim. 1907, 26, 228). *Malonylazoimide* $CH_2(CO\cdot N_3)_2$, an explosive oil, is converted into methylenediurethane, $CH_2(NHCO_2Et)_2$, on treatment with alcohol (Curtius, J. pr. Chem. 1895, [ii.] 52, 210).

Ethylenemalonamide $CH_2<\substack{CO\,NH\\CO\,NH}>C_2H_4$, from ethylenediamine and malonamide at 170°–180° (Freund, *l.c.*); o-*phenylenemalonamide* and o-*tolylenemalonamide* melt above 300° (Meyer, Annalen, 1906, 347, 17).

Malonylcarbamide, barbituric acid (2:4:6-di-ketohexahydropyrimidine), *v.* PYRIMIDINES.

Hydrazides. *Malonhydrazide*

$$CH_2(CONH\cdot NH_2)_2$$

crystallises in needles, m.p. 154°; for condensation products with aldehydes and alkyl acetoacetates, *see* Curtius, Schöfer and Schwan (J. pr. Chem. 1895, [ii.] 51, 180); Ruhemann (Ber. 1894, 27, 1658); Bulow and Bozenhardt, (Ber. 1909, 42, 4784; 43, 234; 551). *Potassium hydrazino-malonate*, m p. 174°; *benzylidene-hydrazino-malonic acid*

$$CO_2H\cdot CH_2\,CO\cdot NH\cdot N:CHPh$$

m.p. 162° (Curtius and Sieber, Ber. 1921, 54 [B], 1430). *Malonphenylhydrazide*

$$CH_2(CONH\cdot NHPh)_2,$$

m.p. 187° (Goldsmith, *ibid.* 1888, 21, 1240; Asher, *ibid.* 1897, 30, 1018) The phenylhydrazine salt of *phenylhydrazidemalonic acid*

$$PhNH\cdot NH_2\cdot HO_2C\cdot CH_2\cdot CONH\cdot NHPh$$

melts at 141°–143°, and yields the *acid*

$$CO_2H\cdot CH_2\cdot CONH\cdot NHPh$$

m.p. 154° on treatment with acid, and *malonylphenylhydrazide*, $CH_2<\substack{CO\\CO}>N_2HPh$, m.p. 128°, when heated at 200° (Fischer and Passmore, Ber. 1889, 22, 2728).

Malondihydroxamic acid $CH_2(C(OH):NOH)_2$, m.p. 160°, *ammonium malonylhydroxamate*

$$(NH_4)O_2C\cdot CH_2\cdot C(OH):NOH$$

m.p. 181° (Hantzsch, Schatzmann, and Urbahn, Ber. 1894, 27, 804; Pickard, Allen, Bowdler and Carter, Chem. Soc. Trans. 1902, 81, 1572).

Nitriles of malonic acid. The *seminitrile* or *cyanacetic acid* $CN\cdot CH_2\,CO_2H$, prepared by the action of potassium cyanide on chloroacetic acid (Fiquet, Ann. Chim. Phys. 1893, [vi.] 29, 438; Phelps and Tillotson, Amer. J. Sci 1908, iv. 26, 267, 278), forms well-defined large prisms, m.p. 69°–70°. The salts of cyanacetic acid are either amorphous or crystallise with difficulty (Engel, Bull. Soc. chim. [ii.] 44, 225; Meves, Annalen, 1867, 143, 201).

Ethyl cyanacetate $CN\cdot CH_2\cdot CO_2Et$, b.p. 207° (Phelps and Tillotson, *l.c* 261, 257); condenses with carbamide to form the ester,

$$CO<\substack{NH\\NH}>C\cdot CH_2\cdot CO_2Et$$

m.p. 162° (decomp.), soluble in 8333 parts of water at 24°. It gives *m*-toluidine, strychnine, bromine and metallic derivatives. The corresponding *methyl ester* crystallises with $1\frac{1}{2}$ H_2O, m.p. 116° (anhydrous has m p. 128°) and gives similar derivatives to the ethyl ester (Frerichs and Hartwig, J. pr. Chem. 1905, [ii.] 72, 489; *ibid.* 1906, [ii.] 73, 21).

The *sodium* compound of ethyl cyanacetate, $CN\cdot CHNa\cdot CO_2Et$ or $CN\cdot CH:C<\substack{ONa\\OEt}$, forms a neutral solution in water which is not decomposed by hydrochloric acid in the cold. It absorbs iodine rapidly, forming the compound $C_5H_6O_2NI$, and also ethyl dicyanosuccinate, m.p. 120°, as the result of a secondary reaction (Thorpe, Chem. Soc. Trans 1900, 77, 923).

Methyl cyanacetate $CN\cdot CH_2\cdot CO_2Me$ is a colourless liquid, b.p. 177° (Fenton, Chem. Soc. Trans. 1900, 1297). *Menthyl cyanacetate*

$$CN\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$$

flattened needles, m p. 83°–84°, $[\alpha]_D - 81\cdot12°$ (2 p.c. solution in benzene); the monobromo-derivative has m.p. 134°–135° (Bowack and Tapworth, Chem. Soc Proc. 1903, 22). o-*Tolylcyanacetate* $CN\cdot CH_2\cdot CO_2\cdot C_6H_4Me$, prisms, m.p 70·4° (Haller, Compt. rend. 1889, 108, 1116).

Cyanacetamide $CN\,CH_2\,CONH_2$ forms hexagonal tablets, m.p. 120° (Hesse, Amer. Chem. J. 18, 724; Errera, Gazz. chim. ital. 27, ii. 412; Sachs, Ber. 1900, 33, 964: Fiquet, *l.c.*). *Cyanacetanilide*, $CN\cdot CH_2\cdot CONH\cdot C_6H_5$, m.p. 198·5°–200° (Quenda, Atti R. Accad. Sci. Torino, 27). The fluorine derivative

$$CN\cdot CH_2\cdot CONH\cdot C_6H_4F$$

has m.p. 150°–151° (Wallach and Heusler, Annalen, 1888, 243, 223). *Cyanacetdiphenylamide* $CN\cdot CH_2\cdot CO\cdot N(C_6H_5)_2$, has m.p. 153°–154° (Guareschi, Atti R. Accad. Sci. Torino, 27). *Cyanacet*-p-*tolylamide*, $CN\cdot CH_2\cdot CONH\cdot C_7H_7$, m.p 180° (Grothe, Arch. Pharm. 823, 608).

Cyanacetxylylamide

$$CN\cdot CH_2\cdot CONH\cdot C_6H_3(CH_3)_2$$

has m.p. 167°.

Cyanacetpiperidide, $CN\cdot CH_2\cdot CONC_5H_{10}$, forms large prisms, m.p. 88°–89° (Guareschi, *l.c.*).

Cyanacetphenocoll

$$OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NHCO{\cdot}CH_2{\cdot}CN$$

white crystals, m.p. 28°.

Cyanacetylanisidine

$$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$$

m.p. 136°, and *Cyanacetyl*-p-*aminophenetole* $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CN$, m.p. 180°–181°, yield the corresponding oxamic acid on oxidation (Nicola, Ann. Chim. Farm. 18, 353).

Cyanoacetylhydrazine $CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, m.p. 114·5°–115°. With aldehydes it yields the compounds $CN{\cdot}CH_2{\cdot}CONH{\cdot}N:CHR$, with ketones, the compounds $CN{\cdot}CH_2{\cdot}CONHN.CRR'$.

Cyanacetylacetylhydrazine,

$$CN{\cdot}CH_2{\cdot}CONH{\cdot}NH{\cdot}CO{\cdot}CH_3$$

has m.p. 172°.

Cyanacetyl phenylsulphonylhydrazine

$$CN{\cdot}CH_2{\cdot}CONH{\cdot}NH{\cdot}SO_2C_6H_5$$

is formed by the action of benzenesulphonic chloride on cyanacetylhydrazine (Rothenberg, Ber. 1894, 27, 1894).

Cyanacetylcyanamide $CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CN$, m.p. 93° (D. R. P. 167138, Chem. Zentr. 1906, i. 797).

Cyanacetylcarbamide $CN{\cdot}CH_2{\cdot}CONH{\cdot}CO{\cdot}NH_2$, m.p. 212° (decomp.). The *methyl carbamide*, m.p. 206°, the *phenyl*, m.p. 216°, and other alkyl derivatives are described (D. R. P. 175415; Chem. Zentr. 1906, ii. 1590; Baum, Ber. 1908, 41, 532; Conrad and Schulze, Ber. 1909, 42, 735). They are employed technically in the production of the purine bases.

Cyanacetylurethane

$$CN{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO_2Et$$

m.p. 167°–168° (Conrad and Schulze, *l.c.*).

Malonodinitrile $CH_2(CN)_2$ (Henry, Compt. rend. 1886, 102, 1394; Hesse, Amer. Chem. J. 1896, 18, 726) is a colourless crystalline compound, m.p. 29°–30°, b.p. 218°–219°/760 mm. (Henry); b.p. 99°/11 mm. or 109°/20 mm., soluble in 7·5 parts water, 2·5 parts alcohol, 5 parts ether, 10 parts chloroform, or 15 parts benzene (Hesse); forms the mono- and di- silver salts $CHAg(CN)_2$ and $CAg_2(CN)_2$ (Hesse), and reacts with hydroxylamine (1 mol.) to form *cyanethenylamidoxime*

$$CN{\cdot}CH_2{\cdot}C(NH_2):NOH$$

m.p. 124°–127° with decomposition, and yields an *acetyl* and *benzoyl* derivative, m.p. 142° and 184°–192° respectively; *malonodiamidoxime* $CH_2[C(NH_2):NOH]_2$ melts and decomposes at 163°–167°, and yields a *diacetyl* and *dibenzoyl* derivative, m.p. 153°–159° and 183°–185° respectively (Schidtmann, Ber. 1896, 29, 1168). For the action of nitrous acid on malononitrile *see* Diels and Borgwardt (Ber. 1921, 54 [B], 1334).

Aldehydes of malonic acid. The *semialdehyde*, $CHO{\cdot}CH_2{\cdot}CO_2H$, obtained by Wohl and Emmerlich (Ber. 1900, 33, 2760) from β-chloropropionacetal $CH_2Cl{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ is not stable and its physical constants have not been determined. The *amide* $(CHO{\cdot}CH_2{\cdot}CONH_2)$ obtained by Langheld (Ber. 1909, 42, 2360) by the action of sodium hypochlorite on asparagine, is not a stable compound but yields a *phenylhydrazone* $C_9H_{11}ON_3$, m.p. 239°–240°. The *nitrile* or *cyanacetaldehyde* $CN{\cdot}CH_2{\cdot}CHO$ is a colourless, limpid, volatile inflammable liquid of b.p. 71·5° (Chautard, Ann. Chim. Phys. 1889, [vi.] 16, 176).

The dialdehyde and semialdehyde of malonic acid are stated to be among the products formed when the ozonide peroxides of α- or β-linolenic acids are decomposed by boiling with water (Erdmann, Bedford and Raspe, Ber. 1909, 42, 1334).

Malonic acid halides. *Malonic semichloride* $CO_2H{\cdot}CH_2{\cdot}COCl$, m.p. 65° with decomposition, obtained by the action of thionyl chloride on an ethereal solution of malonic acid, is unstable (Staudinger and Ott, Ber. 1908, 41, 2208); the *methyl ester* has b.p. 57°–59° (Staudinger and Becker, Ber. 1917, 50, 1016); the *ethyl ester* $COCl{\cdot}CH_2{\cdot}CO_2Et$, has b.p. 170°–180°, (Van 't Hoff, Ber. 1874, 7, 1572), or 68°–70°/13 mm., loses HCl at 125°–130°, and yields the *compound* $C_{13}H_{12}O_8$, yellow prisms, m.p. 170°–180° (corr.) (Marguery, Bull. Soc. chim. 1900, [3] 33, 541; Leuchs, Ber. 1906, 39, 2641). The *nitrile* or *cyanacetylchloride* $CN{\cdot}CH_2{\cdot}COCl$, was prepared by Mulder (Bull. Soc. chim. [ii.] 29, 533). *Malonyl chloride* $CH_2(COCl)_2$, obtained when malonic acid is mixed with an excess of thionyl chloride and distilled under reduced pressure (Staudinger and Bereza, Ber. 1908, 41, 4461), and yields carbon suboxide (*q.v.*) when treated with silver or lead oxide (Staudinger and Bereza, *l.c.*), is a colourless liquid, b.p. 58°/27 mm. (Auger, Ann. Chim. Phys. 1891, [vi.] 22, 325). For the constitution of the chloride *v.* Auwers and Schmidt (Ber. 1913, 46, 457). *Malonyl bromide* $CH_2(COBr)_2$, b.p. 55–57/11 mm. (Fleischer, Hittel and Wolff, Ber. 1920, 53 [B], 1847.

The *seminitrile* of *malonyl bromide*, *cyanacetylbromide*, crystallises in the monoclinic system, and has m.p. 77°–79° (Hübner, Annalen, 1864, 131, 66)

SUBSTITUTED MALONIC ACIDS AND DERIVATIVES.

Alkyl malonic acids. The hydrogen atoms of the methylene group in ethyl malonate can be replaced by sodium (Conrad, Annalen, 1880, 204, 129; Ballo, Ber. 1881, 335); ethyl sodiomalonate, $CO_2Et{\cdot}CH{<}\begin{smallmatrix}ONa\\OEt\end{smallmatrix}$ (Meyer, Ber. 1912, 45, 2861), is a colourless crystalline compound; it does not undergo dissociation in alcoholic solution (Vorlander and Schilling, *ibid.* 1899, 32, 1876); is not stable in the presence of water, and yields no colour with ferric chloride (Vorlander, *ibid.* 1903, 36, 268). It condenses with alkyl and aryl halides to form the alkyl or aryl substituted malonic ester, the sodio-derivative of which yields on similar treatment the di-substituted ester (Bischoff, *ibid.* 1895, 28, 2616). For the mechanism of these reactions *see* Jackson and Whitmore (J. Amer. Chem. Soc. 1915, 37, 1522, 1915). The corresponding substituted malonic acids can be obtained by hydrolysis of the esters, and these lose carbon dioxide when heated above their melting-point with the formation of the corresponding acid of the acetic series:

$$\begin{aligned}CH_2(CO_2Et)_2 &\rightarrow CHR(CO_2Et)_2 \rightarrow CRR'(CO_2Et)_2\\ &\rightarrow CRR(COOH)_2 \rightarrow CHRR'{\cdot}COOH\end{aligned}$$

With the exception of diethylmalonic acid, which is employed in the synthetic preparation of certain pyrimidines of therapeutic value, a description of the numerous alkyl malonic acids does not come within the scope of this article. For the identification of the acids by means of their *p*-nitrobenzylesters, *v.* Lyman and Reid (J. Amer Chem. Soc 1917, 39, 701).

Diethylmalonic acid $\mathrm{CEt_2(CO_2H)_2}$, m.p. 112°; the *anhydride* $[\mathrm{CEt_2}<^{\mathrm{CO}}_{\mathrm{CO}}>\mathrm{O}]_n$, has m.p. 95°–97° (Staudinger and Ott, Ber. 1908, 41, 3829); the *quadrimolecular anhydride* has m.p. 220° (Einhorn and Diesbach, Ber. 1906, 39, 1222), and a liquid *anhydride* is described by Ott (Ann. 1913, 401, 159); the *ethyl ester* has b.p. 228·5°–229·5° (corr.) (Michael, J. pr. Chem. 1905, [ii.] 72, 537), for its absorption spectra *v.* Brannigan, Macbeth, Stewart (Chem. Soc. Trans 1913, 103, 406); *methyl ester* has b.p. 204°–205° (Meyer, Ber. 1906, 39, 198); p-*nitrobenzyl ester*, m p. 91·2° (Layman and Reid, J. Amer. Chem. Soc. 1917, 39, 701); *diethylmalonate of glycollamide* $\mathrm{CEt_2(CO{\cdot}O{\cdot}CH_2{\cdot}CO{\cdot}NH_2)_2}$, has m.p. 126°; *diethylaminoethyl diethylmalonate*

$$\mathrm{CEt_2(CO{\cdot}OCH_2{\cdot}CH_2{\cdot}NEt_2)_2}$$

(Einhorn, Annalen, 1908, 359, 145); *ethyl diethylmalonamate*, has m.p. 79° b.p. 263° (D. R. P. 182045); *trichlorbutyl hydrogen diethylmalonate* has m p 100° (D. R. P. 289001); *diethylmalonamic acid*, m.p. 146°, *diethylmalondiethylamic acid* $\mathrm{NEt_2CO{\cdot}CEt_2{\cdot}CO_2H}$, m p. 88°–90° (Einhorn and Diesbach, Ber. 1906, 39, 1222); *diethylmalonamide*, m.p. 224° (corr.) (Fischer and Dilthey, *l c.*), forms a crystalline compound, $\mathrm{CEt_2(CONH_2)_2{\cdot}CCl_3{\cdot}CHO}$, m.p. 178° with chloral hydrate (Burrows and Keane, Chem. Soc. Trans. 1907, 91, 269). *Diethylmalonylmalonamide* has m.p. 175°–176°, *diethylmalonylmethylmalonamide* has m.p. 118°–119°; *diethylmalonylethylmalonamide*, m.p. 88°–89°; *diethylmalonylbenzidine*, m.p. 224° (Remfry, *l.c.*). *Diethylmalonylmonophenylamide* $\mathrm{NH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NHPh}$, m.p 132° the *sulphanilide* $\mathrm{NH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H}$, has a strong acid reaction and decomposes carbonates, *diethylmalonanilic acid*

$$\mathrm{NHPh{\cdot}CO{\cdot}CEt_2{\cdot}CO_2H}$$

m.p. 105° (Conrad and Zart, Annalen, 1905, 340, 335). *Diethylmalonyl*-p-*phenetidine*

$$\mathrm{CEt_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}OEt)_2}$$

m.p. 143°, has antipyretic properties and exerts a soporific action (D. R. P. 165311). *Diethylmalonyldiurethane* $\mathrm{CEt_2(CO{\cdot}NH{\cdot}CO_2Et)_2}$, a thick oil (Traube, D. R. P. 179946); *ureide of diethylmalonic acid* $\mathrm{CO_2H{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2}$, m.p. 162° (corr.) (Fischer and Dilthey, Annalen, 335, 334); *ethyl diethylmalonylureide*

$$\mathrm{CO_2Et{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2}$$

m.p. 85°; *methyldiethylmalonylureide*, m.p. 115° (Boehringer and Sohne, D. R. P. 193447); *diethylmalonyluramide*

$$\mathrm{NH_2{\cdot}CO{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2}$$

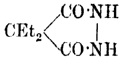
m.p. 199° (Conrad and Zart, *l.c.*); *diethylmalonyltetramethyldicarbamide*

$$\mathrm{CEt_2(CO{\cdot}NH{\cdot}CO{\cdot}NMe_2)_2}$$

m.p. 158°; *diethylmalonyltetraethyldicarbamide*, m p. 123°–126° (Einhorn, D. R. P. 193446). *Diethylmalonylanthranilamide*

$$\mathrm{CEt_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}CONH_2)_6}$$

m.p. 215° Cyclo*Diethylmalonylhydrazide*



$$\mathrm{CEt_2}\begin{cases}\mathrm{CO{\cdot}NH}\\ \quad\ \ |\\ \mathrm{CO{\cdot}NH}\end{cases}$$

m.p. 256° (Einhorn, Annalen, 1908, 359, 145). *Diethylmalonodinitrile* $\mathrm{CEt_2(CN)_2}$, m.p. 44°, b.p. 195°–195·5° (Hesse, Amer. Chem. J. 1896, 18, 723; Errera and Berté, Gazz. chim. ital. 1896, 26, ii. 220). The *seminitrile of diethylmalonic acid* (*diethylcyanacetic acid*)

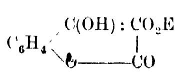
$$\mathrm{CN{\cdot}CEt_2{\cdot}CO_2H}$$

has m p. 57°, b.p. 162°–164°/18 mm., the *ethyl ester*, b.p 215°–216°, 100°–101°/14 mm. (Hesse, Amer. Chem. J. 1896, 18, 723; Hessler, *l.c.* 171). *Diethylcyanacetamide* $\mathrm{CN{\cdot}CEt_2{\cdot}CONH_2}$, colourless plates, m.p. 120° (Hesse). *Diethylmalonic semichloride* is an oil (Staudinger and Ott, Ber. 1908, 41, 2208); *diethylmalonyl chloride* $\mathrm{CEt_2(COCl)_2}$, has b.p. 196·5°–197·5° (Fischer and Dilthey, Ber. 1902, 38, 844).

Acyl malonic esters. The acyl derivatives of malonic esters are prepared by the condensation of the sodiomalonic ester with the acyl chloride; the corresponding acids are not known. For the constitution of the esters *see* von Auwers and Auffenberg (Ber. 1917, 50, 929).

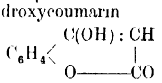
The acetyl, diacetyl, phenacetyl, diphenacetyl, propionyl, butyryl, benzoyl, nitrobenzoyl, succinyl, adipyl, phthalyl, and camphoryl malonic esters and derivatives have been prepared, *see* Michael, Amer. Chem. J. 1892, 14, 481; Schott, Ber. 1896, 29, 1985; Guinchant, Bull. Soc chim. 1895, [iii.] 13, 1029; Held, Compt rend. 116, 720; Lang, Ber. 1887, 20, 1326; Knoevenagel and Faber, Ber. 1898, 31, 2771; Claisen, Annalen, 1896, 291, 72; Bischoff and Rach, Ber. 1884, 17, 2793; Haller, Bull. Soc. chim [ii.] 45, 271; Barthe, *ibid.* [iii.] 21, 529; Scheiber, Ber. 1909, 42, 1318; Wislicenus, Annalen, 1887, 242, 23; Wislicenus and Winzer, Annalen, 1890, 257, 298; Baeyer, Ber. 1892, 25, 1039; Ingle, Ber 1894, 27, 2526.

Ethyl sodiomalonate condenses with acetyl salicylyl chloride or ortho substituted salicylylchlorides to form ethyl β-hydroxycoumarin-α-carboxylate



$$\mathrm{C_6H_4}\begin{cases}\mathrm{C(OH):CO_2Et}\\ \qquad\qquad\ |\\ \mathrm{O}\text{———}\mathrm{CO}\end{cases}$$

or the corresponding ortho-substituted derivatives; the acids obtained from these compounds by hydrolysis lose carbon dioxide and yield the β-hydroxycoumarin



$$\mathrm{C_6H_4}\begin{cases}\mathrm{C(OH):CH}\\ \qquad\qquad |\\ \mathrm{O}\text{———}\mathrm{CO}\end{cases}$$

or an ortho-substituted derivative, substances of potential therapeutic value.

Ethyl β-hydroxycoumarin-α-carboxylate has m.p. 93°; *β-hydroxycoumarin* has m.p. 206°; *ethyl 3 : 5-dichloro-β-hydroxycoumarin-α-carboxylate* has m.p. 135°, and *3 : 5-dichloro-β-hydroxycoumarin* has m.p. 275° (Aktien Gesellschaft für Anilinfabrikation, D. R. P. 102096, 1899; *cf.* Anschütz, Ber. 1903, 36, 463).

Chloro, bromo, and iodo malonic acids. Malonic acid, its esters, amides and substituted amides react readily with chlorine or bromine, forming under suitable conditions the mono- and di-halogen derivatives. The halogen in certain of these compounds is highly reactive and liberates iodine from hydrogen iodide with the regeneration of the malonic compound according to the equation

$$(CONH_2)_2CBr_2+4HI$$
$$=(CONH_2)_2CH_2+2HBr+2I_2$$

The reaction is in most cases quantitative and affords a rapid means of estimating the halogen in the compound (Whiteley, Chem. Soc. Proc. 1908, 24, 278; and Backes, West and Whiteley, Chem. Soc. Trans. 1921, 119, 359).

Chloromalonic acid $CHCl(CO_2H)_2$, m.p. 133° (Conrad and Guthzeit, Ber. 1882, 15, 605), the *ethyl ester*, b.p. 137°–139°/50 mm., sp.gr. 1·1776 at 20°/4°, n_D 1·4327 at 20° (Bruhl, J. pr. Chem. [ii.] 50, 140); b.p. 91°/2 mm. (Forster and Muller, Chem. Soc. Trans. 1910, 97, 126); the *seminitrile* or *ethyl chlorocyanacetate*

$$CN\cdot CHCl\cdot CO_2Et$$

b.p. 190° (Henry, Compt. rend. 1887, 104, 1618). *Chloromalonamide* $CHCl(CONH_2)_2$, m.p. 170° (Conrad and Bischoft, Annalen, 209, 231); *chloromalondimethylanilide* $CHCl(CONMePh)_2$, m.p. 181°, and *chloromalontetraphenylamide* $CHCl(CONPh_2)_2$, m.p. 213° (Whiteley). *Chloromalonaldehyde* $OH\cdot CH:CCl\cdot CHO$, m.p. 144°, gives with aniline, the *monoanilide*

$$NHPh\cdot CH:CCl\cdot CHO$$

m.p. 193° (Dieckmann and Platz, Ber. 1904, 37, 4638).

Dichloromalonic acid $CCl_2(CO_2H)_2$ (Dootson, Chem. Soc. Trans. 1899. 169); the *aniline salt* has m.p. 105° (Conrad and Reinbach, Ber. 1902, 35, 1813); the *ethyl ester*, b.p. 231°–234°, sp.gr. 1·268 at 17°/15° (Conrad and Bruckner, *ibid.* 24, 2993); the *methyl ester*, b.p. 110°–120°/20 mm., (Zincke, Kegel, *ibid.* 1890, 23, 244). *Dichloromalonamide*, m.p. 204° (Conrad and Bruckner, *l.c.*; Zincke and Kegel, *l.c.*).

Bromomalonic acid $CHBr(CO_2H)_2$ (Petrieff, Ber. 1878, 11, 414; Conrad and Reinbach, Ber. 1902, 35, 1813; Lutz, Ber. 1902, 35, 2549; Biilmann and Madsen, Annalen, 1914, 402, 331) crystallises in plates, m.p. 113°; the *barium salt*, and the *silver salts* are crystalline. *Methyl bromomalonyl chloride*, b.p. 90°–91°/10 mm. (Staudinger and Becker, Ber. 1917, 50, 1016). *Methyl bromomalonate* $CHBr(CO_2Me)_2$ is a colourless mobile liquid, b.p. 145°/22 mm. (Kohler, Heritage, McLeod, Amer. Chem. J. 1911, 46, 234). *Ethyl bromomalonate* $CHBr(CO_2Et)_2$, b.p. 223°–235° with slight decomposition (Knoevenagel, Ber. 1888, 21, 1356), 118°–119°/11 mm. (private communication); 150°–152°/25 mm. (Bischoff, Ber. 1907, 40, 3134); sp.gr. 1·426 at 15° (Conrad and Bruckner, Ber. 1891, 24, 2997); *methyl bromomalonate* $CHBr(CO_2Me)_2$, b.p. 112·5°–113°/15 mm. (Bischoff, *l.c.*) *Bromomalonamide* $CHBr(CONH_2)_2$, m.p. 181° *Bromomalondiurethane* $CHBr(CO\cdot NH\cdot CO_2Et)_2$, m.p. 148° (Backes, West and Whiteley, *l.c.*).

For the *bromomalon*-alkyl-*amides*, and the *bromomalon*-aryl-*amides* and their brominated derivatives, *see* Backes, West and Whiteley (*l.c.*).

Methyl bromomalonanilate, m.p. 113°–114° (Staudinger and Becker, *l.c.*).

The *seminitrile* or *bromocyanacetic acid* $CN\cdot CHBr\cdot CO_2H$ (Petrieff, J. Russ. Phys. Chem. Soc. 10, 160). *Ethyl bromcyanacetate*, b.p. 116°/25 mm. (Nef, Annalen, 1897, 298, 202).

Bromomalonitrile $CHBr(CN)_2$, has m.p. 65°–66° (Hesse, Amer. Chem. J. 1896, 18, 723).

Bromomalonaldehyde $OH\cdot CH:CBr\cdot CHO$, m.p. 140°; the *anilide* $NHPh\cdot CH:CBr\cdot CHO$, has m.p. 184°: the *dianilide hydrobromide*

$$NHPh\cdot CH:CBr\cdot CH:NHPh,HBr$$

crystallises with EtOH and has m.p. 217° (Lespieau, Compt. rend. 1901, 133, 538).

Dibromomalonic acid $CBr_2(CO_2H)_2$ (Petrieff, Ber. 1874, 7, 400; Willstatter, Ber. 1902, 35, 1374; Conrad and Reinbach, Ber. 1902, 35, 1813) has m.p. 130°–131° (Willstatter), or 147° (Conrad and Reinbach); the heat of solution is +2·02 cal *Potassium hydrogen dibromomalonate* forms brilliant anhydrous crystals, heat of dissolution −5·60 cal.; the *potassium salt* becomes anhydrous at 100°, decomposes at 200°, and has heat of dissolution − 9·94 cal. (Massol, Compt rend. 1892, 114, 1200); the crystalline *aniline* salt melts at 113° (Conrad and Reinbach, *l.c.*). *Methyl dibromomalonate* $CBr_2(CO_2Me)_2$, m.p. 63°–65°; *ethyl dibromomalonate* has b.p. 145°–155°/25 mm. (Conrad and Brückner, Ber. 1891, 24, 3001), b.p. 126°–131°/14 mm. (Reitter and Weindel, *ibid.* 1907, 40, 3358); 135°–137°/13 mm. (Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1003); b.p. 134°/12 mm (private communication). *Dibromomalonamide*

$$CBr_2(CONH_2)_2$$

m.p 203° (Backes, West and Whiteley, *l.c.*), *dibromomalondimethylamide*

$$CBr_2(CONHMe)_2$$

m.p. 162° (Freund, Ber. 1884, 17, 780); *dibromomalonanilide* $CBr_2(CONHPh)_2$, m.p. 147° (Staudinger and Bereza, Ber. 1908, 41, 4465; Backes, West and Whiteley, *l.c.*).

For other *dibromomalon*-alkyl-*amides*, and *dibromomalon*-aryl-*amides* and their brominated derivatives, *see* Backes, West and Whiteley, *l.c.*

Dibromomalonitrile $CBr_2(CN)_2$, m.p. 123·5°–124° (Hesse, Amer. Chem. J. 1896, 18, 723). *Dibromomalonylchloride* $CBr_2(COCl)_2$, has b.p 75°–77°/15 mm., and solidifies at the ordinary temperature (Staudinger and Bereza, Ber. 1908, 41, 1461), *dibromomalonylbromide*

$$CBr_2(COBr)_2$$

has b.p. 91°–92°/13 mm. (Staudinger and Klever, *ibid.* 1908, 41, 906)

Iodomalondimethylanilide

$$CHI(CONMePh)_2$$

has m.p 164° (Vorlander and Herrmann, Ber. 1898, 31, 1826).

Di-iodomalonic acid $CI_2(CO_2H)_2$, is very unstable; it crystallises in pale yellow leaflets, m.p. 119°–120°. The *methyl ester* crystallises in pale yellow needles, m.p. 79°–80° (Willstätter, Ber. 1902, 35, 1374).

Ethyl chlorobromomalonate $CClBr(CO_2Et)_2$, has b.p. 136°–139°/35 mm., sp.gr. 1·467 at 16°/15° (Conrad and Brückner, Ber. 1891, 24, 2993); the *methyl ester* is crystalline, m.p. 40°–42° (Bischoff, Ber 1907, 40, 3150).

Derivatives of cyanomalonic acid. *Ethyl cyanomalonate* $CN\cdot CH(CO_2Et)_2$, is a colourless oil, b.p 120°–130°/25 mm., with a pungent smell and acid reaction, and forms crystalline soluble salts. *Methyl cyanomalonate* also yields crystalline metallic derivatives (Haller, Compt. rend. 1882, 95, 142; Ann. Chim. 1889, [vi.] 16, 403). The *ethyl ester* of the *seminitrile* (*ethyl dicyanacetate*) $(CN)_2CH\cdot CO_2Et$ is crystalline, and forms crystalline sodium, silver and copper salts. The methyl ester is also known (Haller, Compt. rend. 1890, 111, 53).

Ethyl dicyanomalonate or *ethyl cyaniminoisosuccinate* $NH:C(CN)\cdot CH(CO_2Et)_2$, colourless needles, m.p. 93°.

Derivatives of triazomalonic acid. *Ethyl methyltriazomalonate* $CH_3\cdot CN_3(CO_2Et)_2$, is a colourless liquid, b.p. 69°/0·6 mm., sp.gr. 1·11695 at 16°/16°; *methyltriazomalonamide* $CH_3\cdot CN_3(CONH_2)_2$, m.p. 137·5°; *methyltriazomalonic acid* $CH_3\cdot CN_3(CO_2H)_2$, m.p. 87·5°; *ethyl triazomalonic acid* $C_2H_5\cdot CN_3(CO_2H)_2$, melts and decomposes at 105°–107°; the *ethyl ester* has b.p. 83·5°/0·7 mm., sp.gr. 1·1161 at 16°/10°; the *amide* has m.p. 167°.

Phenyltriazomalonic acid $C_6H_5\cdot CN_3(CO_2H)_2$, m.p. 99°; the *ethyl ester* decomposes on attempted distillation, the *amide* has m.p. 189°. *Ethyl bistriazomalonate* $C(N_3)_2(CO_2Et)_2$, has b.p. 115°–115·5°/0·81 mm., sp.gr. 1·2136 at 20°, and is decomposed violently by sulphuric acid; the *amide* melts at 162° with vigorous decomposition (Forster and Muller, Chem. Soc. Trans. 1910, 97, 126).

Aminomalonic acid and derivatives. *Aminomalonic acid* $H_2N\cdot CH(CO_2H)_2,H_2O$, m.p. 109° (Baeyer, Annalen, 131, 291; Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1007; Lutz, Ber. 1902, 35, 2549); *ethyl aminomalonate hydrochloride* $H_2N\cdot CH(CO_2Et)_2,HCl$, forms colourless needles, m.p. 162° (decomp.). The hydrochloride of the *methyl ester* melts and decomposes at 159°. *Aminomalonamide* $H_2N\cdot CH(CONH_2)_2$, m.p. 192° (Conrad and Guthzeit, Ber. 1882, 15, 605; Piloty and Neresheimer, *ibid.* 1906, 39, 514). *Aminomalonanilide* $(CO\cdot NHPh)_2CH\cdot NH_2$, m.p. 141°–142°; *aminomalondimethylanilide* $(CONMePh)_2CH\cdot NH_2$, m.p. 108°; *aminomalontetraphenylamide* $(CONPh_2)_2CH\cdot NH_2$, m.p. 200°–201°, are obtained by reducing the corresponding *iso*nitroso derivatives (Whiteley, Chem. Soc. Proc. 1904, 92).

Methyl formylaminomalonate

$$CHO\cdot NH\cdot CH(CO_2Me)_2$$

m.p. 85°, b.p. 250° (decomp.); the *ethyl ester* has m.p. 48°; the *amide* has m.p. 206° (decomp.) (Conrad and Schulze, Ber. 1909, 42, 729).

Diaminomalonamide $C(NH_2)_2(CO\cdot NH_2)_2$ (Conrad and Brueckner, Ber. 1891, 24, 2993; Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1002) loses ammonia and yields *iminomalonamide* $NH:C(CO\cdot NH_2)_2$ when carefully heated at 90°–100°. *Methyl tetramethyldiaminomalonate* $C(NMe_2)_2(CO_2Me)_2$, has m.p. 83°–85°, and yields on hydrolysis *tetramethyldiaminomalonic acid*, m.p. 133° (Willstatter, Ber. 1902, 35, 1378).

Iminodimalonamide

$$(H_2N\cdot OC)_2CH\cdot NH\cdot CH(CONH_2)_2$$

decomposes without fusion (Conrad and Guthzeit, Ber. 1882, 15, 605).

Anilinomalonic acid $NHPh\cdot CH(CO_2H)_2$, m.p. 118°–119° (Reissert, Ber. 1898, 31, 382; Conrad and Reinbach, *ibid.* 1902, 35, 511). *Ethyl anilinomalonate* $NHPh\cdot CH(CO_2Et)_2$, m.p. 44°–45° (Curtiss, Amer. Chem. J. 1897, 19, 691), yields indoxylic acid when heated (Blank, Ber. 1898, 31, 1812).

Methyl anilinomalonate, m.p. 68°; the *hydrochloride* has m.p. 133°–135°; the *amide*, m.p. 156°.

Ethyl p-*toluidinomalonate* and *ethyl β-naphthylaminomalonate* melt at 55° and 88° respectively and yield indoxylic acid derivatives when heated (Blank, Ber. 1898, 31, 1812).

Anilinomalonanilic acid

$$NHPh\cdot CH(CO_2H)(CO\cdot NHPh)$$

melts and decomposes at 157° (Reissert, *l.c.*). *Anilinomalonanilide*, m.p. 246°–247° (Wislicenus and Münzesheimer, Ber. 1898, 31, 551).

Ethyl dianilinomalonate $(NHPh)_2C(CO_2Et)_2$, m.p. 117°–118° (Curtiss, Amer. Chem. J. 1897, 19, 691); *methyl dianilinomalonate*, m.p. 124°–125° (Conrad and Reinbach, Ber. 1902, 35, 511).

Aniline dianilinomalonate melts and decomposes at 120° (Conrad and Reinbach, Ber. 1902, 35, 1813).

Methyl phenyliminomalonate

$$PhN:C(CO_2Me)_2$$

is a thick yellow oil, reacting vigorously with water, alcohols, ammonia, amines and acids to form substituted anilinomalonates (Curtiss and Spencer, J. Amer. Chem. Soc. 1911, 33, 985).

Alkyl- and aryl-oxy-malonic acids. *Ethyl ethoxymalonate* $CH(OEt)(CO_2Et)_2$ has b.p. 228° and yields on hydrolysis *ethyl ethoxymalonic acid*, m.p. 123°–125°.

Ethyl diethoxymalonate $C(OEt)_2(CO_2Et)_2$, m.p. 43°–44°, b.p. 228° (Bischoff, Ber. 1897, 30, 487; Curtiss, Amer. Chem. J. 1897, 19, 691).

Ethyl diphenoxymalonate $C(OPh)_2(CO_2Et)_2$, b.p. 250°–260°/60 mm.; the *acid* has m.p. 173°.

Nitrophenoxymalonates. Sodium *o*-, *m*- and *p*-nitrophenoxides react with bromo-malonic esters in benzene or xylene solution according to the equation

$$NO_2\cdot C_6H_4ONa + CXBr(CO_2Y)_2$$
$$NaBr + NO_2\cdot C_6H_4\cdot O\cdot CX(CO_2Y)_2$$

where X = H, Me, Et; Y = Me, Et; and sodium nitrophenoxides condense with methyl and ethyl dibromomalonates yielding bisnitrophenoxymalonic esters $(COOR)_2C(O\cdot C_6H_4NO_2)_2$ (Bischoff, Ber. 1907, 40, 3134, 3150).

Nitromalonic esters and derivatives. *Ethyl nitromalonate* $NO_2\cdot CH(CO_2Et)_2$ is a colourless liquid, b.p. 127°/10 mm., sp.gr. 1·1988 at 20°, 1·220 at 0°; the alkali salts are bright yellow and probably have the *isonitro* structure $(CO_2Et)_2C:NO\cdot OR$ (Wahl, Compt. rend. 1901, 132, 1050; *cf.* Franchimont and Klobbie, Rec. trav. chim. 1889, 8, 283; Hantszch, Ber. 1907, 40, 1523; Curtiss and Kostalek, J. Amer. Chem. Soc. 1911, 33, 962); *methyl nitromalonate* $NO_2\cdot CH(CO_2Me)_2$ forms a crystalline ammonium salt, m.p. 166° (Franchimont and Klobbie, *l.c.*). *Ethyl bromonitromalonate*

$$NO_2\cdot CBr(CO_2Et)_2$$

is a neutral oil, b.p. 136°–137°/11 mm.; the *methyl ester* has b.p. 133°/16 mm. (Willstätter and Hottenroth, Ber. 1904, 37, 1775).

Nitromalonamide $NO_2\cdot CH(CO\cdot NH_2)_2$, forms six-sided colourless prisms, m.p. 172° (with decomposition). The *potassium* salt is colourless, but yields yellow solutions (Ruhemann and Orton, Chem. Soc. Trans. 1895, 67, 1002). *Bromonitromalonamide* $NO_2\cdot CBr(CONH_2)_2$, has m.p. 131°–132° and decomposes on boiling with water yielding bromonitromethane (Ratz, Monatsh. 1904, 25, 687).

Nitromalonanilide $NO_2\cdot CH(CO\cdot NHPh)_2$ (Michael, Ber. 1905, 38, 22; Whiteley, Chem. Soc. Proc. 1904, 93) forms pale yellow leaflets, m.p. 141°–142°.

Nitromalonic aldehyde $CHO\cdot CH(NO_2)\cdot CHO$ has m p. 50°–51°. For its condensation products with amines, hydrazines, and hydroxylamines, *v.* Hill and Torrey, Amer. Chem. J. 1899, 22, 89; Hill and Hale, Amer. Chem. J. 1903, 29, 253.

Ethyl ester of the seminitrile of nitromalonic acid or *ethyl nitrocyanacetate*, $CN\cdot CH(NO_2)CO_2Et$, yields a potassium salt, m.p. 240° (Conrad and Schulze, Ber. 1909, 42, 735). *Nitrocyanacetamide* (fulminuric acid, *q.v.*) $(CN)CH(NO_2)CONH_2$ has m.p. 145° (decomp.) *ibid.* 739.

Nitrocyanacetyl carbamide

$$CN\cdot CH(NO_2)CO\cdot NH\cdot CONH_2$$

is obtained as its potassium salt by the oxidation of the corresponding nitroso compound.

*iso***Nitrosomalonic acid and derivatives.** iso*Nitrosomalonic acid* $(CO_2H)_2C{:}NOH$, m.p. 120°, first obtained by Baeyer by hydrolysis of violuric acid (Baeyer, Annalen, 1864, 131, 292; Conrad and Bischoff, Ber. 1880, 13, 595), is identical with the oxime of mesoxalic acid prepared from mesoxalic acid and hydroxylamine (Meyer and Muller, *ibid.* 1883, 16, 608). *Ethyl* iso*nitrosomalonate* $(CO_2Et)_2C{:}NOH$ (Conrad and Bischoff, Ber. 1880, 13, 595), is a colourless viscid liquid, b.p. 172°/12 mm., sp gr. 1·206 at 4°/0° (Bouveault and Wahl, Compt. rend. 1903, 137, 196); or 1·149 at 15° (Conrad and Bischoff, *l.c.*). *Methyl* iso*nitrosomalonate*, b.p. 168°/13 mm, m.p. 67° (Bouveault and Wahl, *l.c.*). For *oximinomalonamic acid*

$$COOH\cdot C(:NOH)\cdot CONH_2$$

m.p. 137° (decomp.), and *oximinomalonamidine* $CO_2H\cdot C(:NOH)\cdot C(:NH)\cdot NH_2$ (decomposes at 283°), and allied compounds, *v.* Wieland and Baumann, Annalen, 1912, 392, 196.

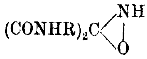
The *iso*nitroso derivatives of malonamide and the substituted amides of malonic acid are obtained by the action of nitrosyl chloride at 0° on the amide dissolved or suspended in dry chloroform, and the yield is usually quantitative.

*iso*Nitrosomalonamide and the alkyl substituted derivatives are colourless, the aryl substituted derivatives are yellow, or exist in two forms one yellow and one colourless, exhibiting dynamic isomerism; all the *iso*nitroso derivatives form crystalline yellow alkali and silver salts, and deep violet or blue ferrous salts. It is probable that the yellow *iso*nitroso derivatives and the salts possess the true oximino structure

$$(CONHR)_2C{:}NOH\,;\ (CONHR)_2C.NOK$$

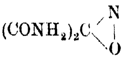
whilst the colourless *iso*nitroso derivatives are

***iso*oximes**



$(CONHR)_2C{<}\begin{matrix}NH\\ |\\ O\end{matrix}$.

iso*Nitrosomalonamide*



$(CONH_2)_2C{<}\begin{matrix}NH\\ |\\ O\end{matrix}$

colourless, m.p. 187° (decomp.); the *acetyl* derivative is colourless, m.p. 190°; *ethyl* derivative, pale yellow, m.p. 150°–151°; the silver salt $(CONH_2)_2C{:}N\cdot OAg,2NH_3$, deep yellow prismatic crystals; *potassium* salt

$$(CO\cdot NH_2)_2C{:}N\cdot OK$$

is yellow, and forms with ferrous sulphate the *ferrous potassium salt*

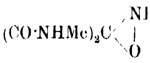
$$(CONH_2)_2\cdot C{:}N\cdot OK,[(CONH_2)_2C{:}N\cdot O]_2Fe$$

which crystallises in well-defined purple prisms with a bronze or green reflex. The *yellow* variety of *iso*nitrosomalonamide

$$(CONH_2)_2C{:}NOH$$

differs from the colourless form only in colour.

iso*Nitrosomalondimethylamide*



$(CO\cdot NHMe)_2C{<}\begin{matrix}NH\\ |\\ O\end{matrix}$

m.p. 157°; the *potassium* salt

$$(CONHMe)_2C{:}N\cdot OK$$

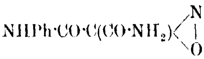
is bright yellow; the *ferrous* salt

$$[(CONHMe)_2C{:}NO]_2Fe$$

is purple.

iso*Nitrosomalonanilide.* The *colourless* variety becomes yellow at 138°–140° and melts at 141°; the *yellow* variety becomes white at 120°–122° and melts at 141°; the equilibrium mixture of the two isomerides melts at 124°.

iso*Nitrosomalonmonophenylamide*



$NHPh\cdot CO\cdot C(CO\cdot NH_2){<}\begin{matrix}NH\\ |\\ O\end{matrix}$

has m.p. 180°–181° (decomp.).

iso*Nitrosomalondi*-p-*tolylamide*

$$(CONH\cdot C_7H_7)_2C{:}N\cdot OH$$

is pale yellow, m.p. 170°–171°; the *colourless* isomeride becomes yellow at 150° and melts at 170°–171°.

iso*Nitrosomalonmono*-p-*tolylamide*

$$C_7H_7\cdot HN\cdot CO\cdot C(CO\cdot NH_2){:}NOH$$

is lemon yellow, m.p. 183°.

iso*Nitrosomalondi-o-tolylamide*

$$(CONH\cdot C_7H_7)_2C{:}NOH$$

is yellow, m.p. 111°; the *colourless* isomeride changes to yellow at 75° and melts at 111°

Ethyl iso*nitrosomalon-o-tolylamate*

$$C_7H_7\cdot HN\cdot CO\cdot C(CO_2Et){:}NOH$$

is pale yellow, m.p. 140°–141°.

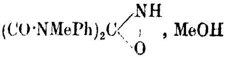
iso*Nitrosomalondi-a-naphthylamide*

$$(CONH\cdot C_{10}H_7)_2C{:}NOH$$

is orange coloured, m.p. 184°.

iso*Nitrosomalondi-β-naphthylamide* is pale yellow, m.p. 221°; the *acetyl* derivative is colourless, m.p. 179° (decomp.).

iso*Nitrosomalondimethylanilide* crystallises with 1 mol. methyl alcohol.



$(CO\cdot NMePh)_2C{<}\begin{matrix}NH\\ |\\ O\end{matrix}$, MeOH

is colourless and has m.p. 109°; the *acetyl* derivative has m.p. 130°, the *benzoyl* derivative m.p. 157°–158°, and the *ethyl ether* m.p. 138°.

iso*Nitrosomalontetraphenylamide*

$$(CONPh_2)_2C{:}NOH$$

forms pale yellow prisms, m.p. 237°–238°

(decomp.); the *acetyl* derivative is pale yellow, m.p. 190°; the *benzoyl* derivative is colourless, m.p. 175°, the *ethyl ether* has m.p. 164°–165°, (Whiteley, Chem. Soc. Trans. 1900, 77, 1040; 1903, 83, 18, 24; Chem. Soc. Proc. 1904, 93).

iso*Nitrosomalondiurethane*

$$(\mathrm{CONH{\cdot}CO_2Et})_2\mathrm{C.NOH}$$

m.p. 203°–204° (Conrad and Schulze, Ber. 1909, 42, 735). The *ammonium* salt forms bright orange prisms, m.p. 174°. The *potassium* salt $(\mathrm{CO{\cdot}NH{\cdot}CO_2Et})_2\mathrm{C.N{\cdot}OK}$, is bright orange-red (Whiteley).

Derivatives of the seminitrile of isonitrosomalonic acid. *Ethyl isonitrosocyanacetate*

$$\mathrm{HON{:}C(CN)CO_2Et}$$

m.p. 133°, yields metallic derivatives (Conrad and Schulze, Ber. 1909, 42, 735).

The *methyl ester* has m.p. 123°. The *ethers*

$$\mathrm{EtON.C(CN)CO_2Et}$$

b.p. 125°–127° 1/22–24 mm. and

$$\mathrm{EtON{:}C(CN)CO_2Me}$$

b.p. 121°–124°/23–25 mm. and the corresponding benzoyl derivative, m.p. 131°–132°, are described by Muller (Ann. Chim. Phys. [vii.] 1, 463).

Isonitrosocyanacetamide (Desoxyfulminuric acid) $\mathrm{CN{\cdot}C{:}NOH{\cdot}CONH_2}$, m.p. 181° (*ibid.* 738).

Isonitrosocyanacetyl carbamide

$$\mathrm{HON{:}C(CN)CO{\cdot}NH{\cdot}CONH_2}$$

m.p. 220° (decomp.) (*ibid.* 741).

Isonitrosocyanacetyl urethane

$$\mathrm{HON{:}C(CN)CO{\cdot}NH{\cdot}CO_2Et}$$

forms white crystals, m.p. 201° (decomp.) (*ibid.* 742).

Condensation of malonic acid with aldehydes. Malonic acid condenses with aldehydes according to the equation

$$(\mathrm{CO_2H})_2\mathrm{CH_2}+\mathrm{OHC{\cdot}R}=(\mathrm{CO_2H})_2\mathrm{C.CHR}+\mathrm{H_2O}$$

The methylene malonic acids thus produced yield the corresponding alkyl or aryl malonic acids $\mathrm{CH_2R{\cdot}CH(CO_2H)_2}$ on reduction; and lose carbon dioxide on heating to form the substituted acrylic acid $\mathrm{CHR{:}CH{\cdot}CO_2H}$.

The *bis*malonic acid $\mathrm{CHR[CH(CO_2H)_2]_2}$ is sometimes obtained when the aldehyde and malonic acid are taken in the proportion of 1 mol. of the former to 2 mols. of the latter.

For the condensation products with formaldehyde, *see* Haworth and Perkin, Chem. Soc. Trans. 1898, 73, 339; Bottomley and Perkin, *ibid.* 1900, 77, 294. For the *ethylidene*, iso*butylidene*, iso*amylidene*, *œnanthylidene*, *valerylidene*, *citrylidene*, *furfurylidene*, *crotonylidene*, *benzylidene*, and *cinnamylidene*, *anisylidene*, *methylsalicylidene*, *piperonylidene* and *phenylpropionylidene* malonic acids and derivatives, *see* Kommenos, Annalen, 1883, 218, 145; Knoevenagel, Ber. 1898, 31, 2585; Braun, Monatsh. 1896, 17, 207; Riedel and Straube, Annalen, 1909, 367, 40; Knoevenagel, D. R. PP. 161171, 156560, 164296, 97735; Verley, Bull. Soc. chim. 1899, [iii.] 21, 414; Dakin, J. Biol. Chem. 1909, 7, 49; Röhmer, Ber. 1898, 31, 281; Riedel, Annalen, 1908, 361, 89; Stuart, Chem. Soc. Trans. 1883, 43, 403; 1885, 47, 155; 1886, 49, 360; Claisen and Crismer, Annalen, 218, 129; Einhorn and Gehrenbeck, Annalen, 1889, 253, 374; Claisen, Ber. 1903, 86, 3664). For condensation with *αβ-di-bromopropaldehyde*, *v.* Lespieaw (Compt. rend. 1910, 151, 1359).

M. A. W.

MALONYLCARBAMIDE, *Barbituric acid*, *v* PYRIMIDINE.

MALT *v.* BREWING.

MALTASE is the enzyme which hydrolyses maltose to two molecules of dextrose. It is present in most, though not in all, species of yeasts; those yeasts (*e.g. Saccharomyces marxianus*, *S. exiguus* (Rees), *S. ludwigii*, *S. saturnus*, *S. anomalus*) which do not contain maltase are unable to ferment maltose. Maltase is found in *Aspergillus niger*, *Penicillium glaucum*, and other mould fungi: a maltose splitting enzyme is present in the intestine (Brown and Heron, Proc. Roy. Soc. 1880, 30, 393) and in numerous other animal tissues (Tebb, J. Physiol. 1894, 15, 421). According to Compton (Biochem. J. 1921, 15, 681) it is present in the blood serum of the dog, pig, goat, horse, and ox, and is absent in that of the cat, guinea-pig, rabbit, and man. Maltase is present in the solid residue left after repeatedly extracting maize, millet, or buckwheat with water until the diastase has been removed. The dry powder has far more powerful enzymatic properties than aqueous extracts, and in this respect resembles the powders from dried leaves containing emulsin, &c., investigated by Armstrong (Proc. Roy. Soc. 1912, 85, B, 363). The maltase so obtained is stated by Wierchowski (Biochem. Zeitsch. 1913, 56, 209, 57, 125) to hydrolyse starch to dextrose and soluble starch, no dextrins being formed as intermediate products. Maltase is more difficult to extract than invertase; active extracts can only be obtained from yeast after the cells have been destroyed, or, better, after a preliminary drying in a thin layer at a low temperature. The enzyme is not liberated on shaking yeast with toluene water. Yeast juice made by Buchner's method of compression contains maltase. Brown and Heron found aqueous extract of pig's intestine to have no action on maltose, but after drying at 35° fine shreds of the intestine were active. Using similar methods Tebb found most maltase in the mucous membrane of the small intestine; it was also present in the spleen, lymphatic gland, liver, kidney, and in the pancreatic and salivary glands, and least of all in muscle. When the tissue is finely minced and sufficient time (several days) is allowed for adequate extraction, active maltase may be obtained from fresh tissues. Malt does not contain maltase.

In preparing maltase solutions for practical work it is always advisable to devote some attention to ascertaining the exact conditions necessary to get a preparation of maximum activity. The yeast should be dried quickly and in thin layers at about 25°, the extract should be prepared with suitable distilled water in hard glass vessels at 35° or less, maceration being continued for not too long a period. The extract should be filtered quickly and used at once. Toluene is by far the best antiseptic to employ.

Maltase is destroyed by precipitation of the aqueous extract with alcohol, so that it has not been possible to purify it.

Maltase also hydrolyses α-methylglucoside and other synthetical α-glucosides, although it is without action on the isomeric β-glucosides. Amygdalin is hydrolysed by an enzyme akin to maltase, present in some yeasts, to dextrose and amygdonitrileglucoside (Fischer, Ber. 1895, 28, 1508). This action is due, however, not to maltase, but to amygdalase (Caldwell and Courtauld, Proc. Roy. Soc. 1907, B, 79, 350). Maltase is able to cause synthetic as well as analytic changes (Croft Hill, Chem. Soc. Trans. 1898, 73, 634; 1903, 83, 578, *see* also Bayliss, The Nature of Enzyme Action, Longmans, 1911).

The optimum temperature of maltase is 35° 40°.

Maltase is destroyed by excess of alkali, and also by acids of any marked strength, a nucleoprotein-like substance being precipitated. The optimum activity as measured towards maltase or α-methyl glucoside takes place in solutions which are just acid, viz. between $p_H = 6{\cdot}1$ and $p_H = 6{\cdot}8$, and in this respect it differs markedly from invertase (optimal point $p_H = 4{\cdot}5$). At this point maltase is inactive and even destroyed. Maltase differs from invertase also in that it is precipitated at its isoelectric point and is adsorbed by kaolin, whereas invertase is not (*cf.* Michaelis and Rona, Biochem Zeitsch. 1913, 57, 70). The activity of maltase solutions is as a rule increased by dialysis, and in such dialysed solutions the optimum activity generally occurs in a solution of lower acid concentration. E. F. A.

MALTHA. A variety of 'mineral tallow' or wax, sp.gr. 0·77, soluble in alcohol, naphtha, and oil of turpentine, said to be originally found on the coast of Finland. It is white, brittle, and stains paper like oil, melts at a moderate heat, and burns with a smoky flame. A similar hydrocarbon is met with in the oil-fields of California.

MALTODEXTRIN *v.* Dextrin.

MALTOSE *v.* Carbohydrates (*cf.* Haworth and Leitch, Chem. Soc. Trans. 1919, 115, 809).

MALVIDIN, MALVIN *v.* Anthocyanins.

MAMMIN *v.* Synthetic drugs.

MANACCANITE. A variety of titaniferous magnetic oxide of iron found in grains and small angular fragments at Manaccan near Helstone, and other places in Cornwall, *v.* Ilmenite; Titanium.

MANCHESTER YELLOW. *Dinitronaphthol* *v.* Naphthalene. Dinitronaphthol-yellow has been used to artificially colour natural saffron. To detect the adulteration, an infusion of the matter is prepared, to which some tartaric acid is added. A hank of wool is then dipped in the boiling solution. The wool thus dyed is washed in very dilute sulphuric acid, and the acid afterwards neutralised with ammonia. If saffron contained any dinitronaphthol, the wool or the solution will be coloured yellow, whereas wool dyed with a decoction of genuine saffron and treated in the same manner becomes colourless (Cazeneuve and G. Ginnossier, J. Soc. Chem. Ind. 5, 437).

MANDELIC ACID (*Phenylglycollic acid*; *α-phenylhydroxyacetic acid*) $C_6H_5{\cdot}CH(OH)CO_2H$. Discovered by Winkler in 1852 in the emulsion of bitter almonds. It may be obtained by warming ω-dibromoacetophenone with dilute alkali (Engler and Wöhrle, Ber. 1887, 2202); by oxidising ω-hydroxyacetophenone with copper sulphate (Breuer and Zincke, *ibid.* 1880, 635); by boiling phenylchloracetic acid with alkali (Spiegel, *ibid.* 1881, 239); and by warming benzoylformaldehyde with alkali (Pechmann, *ibid.* 1887, 2905; Müller and Pechmann, *ibid.* 1889, 2558). It is best prepared by shaking commercial benzaldehyde with a concentrated solution of sodium bisulphite, filtering off and drying the bisulphite compound. This is then made into a paste with water, and the calculated quantity of potassium cyanide solution added with stirring. The oily mandelonitrile soon separates, and is hydrolysed by boiling with three times the theoretical quantity of hydrochloric acid (Pape, Chem. Zeit. 1896, 20, 90; Chem. Fab. vor. Hofmann and Schoetensack, Eng. Pat. 14886; J. Soc. Chem. Ind. 1896, 614; *cf.* Muller, Arch. Pharm. [iii.] 2, 385, 389; Ber. 1872, 980; Wallach, Annalen, 193, 38; Luginin, *ibid.* 139, 299; Winckler, *ibid.* 18, 310).

Forms colourless rhombic prisms; m.p. 118° (Clausen, Ber 1877, 847); sp.gr. 1·361 at 4°/4° (Schroder, *ibid.* 1889, 1612); readily soluble in alcohol and ether. On heating the acid at 200°, benzaldehyde and an amorphous mass is obtained; benzaldehyde, water and diphenylmaleic anhydride are formed when it is heated in a current of air under reduced pressure (Bischoff and Walden, Annalen, 279, 118; Liebig, *ibid.* 18, 312). For the anhydride of mandelic acid $C_{32}H_{26}O_9$, *v.* Stutz, Ber. 1911, 44, 3485. (It is possible that this so-called anhydride is the lactide $(C_8H_6O_2.)$ *Cf.* Denham and Woodhouse, Chem. Soc. Trans. 1913, 1870. Fuming nitric acids yields *o*- and *p*-nitrophenylglycollic acids (Pratesi, Gazz. chim. ital. 21, ii. 402). Electrolysis of an aqueous solution of the potassium salt results in the production of hydrobenzoin and a small quantity of *iso*hydrobenzoin (Walker, Chem. Soc. Trans. 1896, 1279); but according to Miller and Hofer (Ber. 1894, 469) benzaldehyde, carbon dioxide, and carbon monoxide are the products. By passing carbonyl chloride into an ice-cold solution of the acid in pyridine the bimolecular anhydride, m.p. 240°, is formed (Einhorn and Pfeiffer, Ber. 1901, 2951). Hydrogen iodide and phosphorus convert mandelic acid into phenylacetic acid, and fuming hydrochloric acid at 140° yields phenylchloracetic acid. Mandelic acid condenses with phenols in the presence of 73 p.c. sulphuric acid to *o*-hydroxydiarylacetic acid, lactones and *p*-dihydroxydiarylacetic acids (Bistrzycki and Flatau, Ber. 1895, 989; 1897, 124); *v.* also Simonis (Ber. 1898, 2821) for condensation with β-naphthol, resorcinol, and orcinol. The nitrile prepared as above, is a yellow oil, solidifying at −10°. The amide has m.p. 190°, the anilide 151°-152°, and the phenylhydrazide 182° (Tiemann and Friedländer, Ber. 1881, 635; Reissert and Kayser Ber. 1890, 3701; Biedermann, *ibid.* 1891, 4083; Bischoff and Walden, Annalen, 279, 118). The methyl ester has m.p. 52° (Zincke and Brewer, Ber. 1880, 636; Ruhe, *ibid.* 1895, 259), and the ethyl ester has m.p. 34°, b.p. 253°-255° (Michael and Jeanprêtre, Ber. 1892, 1684; Beyer, J. pr. Chem. [ii.] 31, 389); m.p. 37° (McKenzie, Chem. Soc. Trans. 1899, 755).

Mandelic acid contains an asymmetric carbon atom, and hence can be split into two optically active isomerides. Lewkowitsch (Ber. 1882, 1505; 1883, 1565, 2722) obtained *l*-mandelic acid by treating the inactive acid with *Saccharomyces ellipsoideus* (Rees) and *d*-mandelic acid by using various microzoa, such as *Penicillium glaucum*, &c. Partial resolution of the inactive acid has also been effected by means of the fractional crystallisation of salts with alkaloids, such as quinine and morphine, and with active amines such as methylhydrindamine; and by esterification with active alcohols, such as menthol and borneol (McKenzie, Chem. Soc. Trans. 1899, 968; 1904, 378; McKenzie and Thompson, *ibid.* 1905, 1004; Marckwald and Paul, Ber 1906, 3651. Kipping, Chem. Soc. Trans. 1909, 416; Findlay and Hickman, *ibid.* 1909, 1386). Racemisation is found to take place on boiling the active acid with alkali (Holleman, Rec trav. chim. 1898, 17, 323; McKenzie and Muller, Chem Soc. Trans. 1907, 1814). Asymmetric syntheses have been conducted by McKenzie and Humphries (*ibid.* 1909, 1106) from *l*-menthylbenzoylformate, and by Rosenthaler (Biochem. Zeitsch. 1908, 14, 238) from *d*-benzaldehydecyanhydrin. *d*- and *l*-Mandelic acids can also be prepared by the hydrolysis of amygdalinic acid (Dakin, Chem. Soc. Trans. 1904, 1512; *cf.* Wohler, Annalen, 66, 238; Walker, Chem. Soc. Trans. 1903, 83, 472; Tutin, *ibid.* 1909, 663; Feist, Arch. Pharm. 248, 101; Rosenthaler, *ibid.* 105). Incomplete hydrolysis of the ethyl ester by *lipase* yields the *d*-acid, whilst the ester remaining is lævorotatory (Dakin, Chem. Soc. Proc. 1903, 161; J. Physiol. 1903, 30, 253).

l-Mandelic acid has m.p. 132·8°, and $[\alpha]_D - 153{\cdot}1^\circ$ in water (Walden, Zeitsch. physikal. Chem. 1895, 17, 705; *cf.* Lewkowitsch, *l c*; Rimbach, Zeitsch. physikal. Chem. 1899, 28, 251; Ber. 1899, 2385). *d*-Mandelic acid has m.p. 132·8°, and $[\alpha]_D + 156^\circ$ (Kipping, Chem. Soc. Trans. 1909, 416). For experiments on the *Walden Inversion* with mandelic and phenylchloracetic acids, *v.* McKenzie and Clough, Chem. Soc. Trans. 1909, 777.

MANDRAGORA ROOT. In 1889 Ahrens (Annalen, 251, 312) extracted from *Mandragora* root an alkaloid possessing similar physiological properties to atropine, and which he named *mandragorin*. Thoms and Wentzel (Ber. 1898, 31, 2031) showed that the *mandragorin* of Ahrens was a mixture of bases, the chief of which was *hyoscyamine*, and subsequently isolated another base, which they named *scopolamine* (Ber. 1901, 31, 2031). Hesse (J. pr. Chem. 1901, 64, 274) further investigated the subject and found that *mandragora* root contains 0·36 p.c. *hyoscyamine*, 0·04 p.c. *hyoscine* (*scopolamine* of Thoms and Wentzel), 0·01 p.c. *ψ-hyoscyamine*, and a still smaller quantity of a new base *mandragorine*. To obtain these alkaloids, the roots are powdered, moistened with a solution of caustic soda, and extracted with ether under a reflux apparatus. The ethereal solution is repeatedly extracted with dilute sulphuric acid, the acid solution being made alkaline with sodium bicarbonate and extracted with chloroform. This operation is then repeated, whereby the hyoscyamine remains in the aqueous solution. The bases from the chloroform extract are neutralised with hydrobromic acid, and the filtered solution allowed to crystallise. The hydrobromides of the bases are then extracted with acetone, which leaves the pure hydrobromide of hyoscine $C_{17}H_{21}NO_4$ (m.p. 194°). The free base is decomposed by baryta into tropic acid and oscine $C_8H_{13}NO_2$. The mother liquors of the hyoscinehydrobromide yield ψ-hyoscyamine on addition of sodium bicarbonate and extraction with chloroform. On adding sodium carbonate to the residual solution, the alkaloid *mandragorine*, forming a gold double salt $C_{15}H_{19}NO_2HAuCl_4$ is obtained. The free base is decomposed by baryta into atropic acid, and a base resembling tropine.

MANGANATES *v.* MANGANESE.

MANGANESE. Sym. Mn. At.wt. 54·95. (Fr. *Manganèse*; Ger. *Mangan*) Manganese is not found in the metallic state. In combination, especially as oxide, it is widely distributed. The most important ores are those corresponding with the dioxide MnO_2, *pyrolusite*. It is also found as the oxides *braunite* Mn_2O_3, *hausmannite* Mn_3O_4, as hydrated oxide Mn_2O_3,H_2O in *manganite*, and associated with barium oxide in *psilomelane*. As sulphide it occurs as *alabandite* MnS and *hauerite* MnS_2; as carbonate in *rhodocrosite* or *dialogite* $MnCO_3$; as silicate in *rhodonite* $MnSiO_3$; and *tephroite* Mn_2SiO_4. The former is of a beautiful red colour, found largely in the Ural Mountains, and used as an ornamental stone. It is often present to a small extent in other silicates, and confers on them its colour. The chief sources of the manganese ores are Russia, the Caucasus, Brazil, and India. Smaller quantities are mined in Germany, Austria, Spain, Turkey, Japan, Greece, and Hungary. Deposits of manganiferous iron ores occur in California and in the Eastern States of America, Vancouver Island, and Nova Scotia. Manganese deposits are also worked in Cuba. Manganese is present in soils, and frequently in mineral, particularly chalybeate, waters. It occurs in many plants, especially in tea and tobacco, and is, in fact, widely distributed throughout the vegetable kingdom.

Preparation.—Metallic manganese is not used in the arts except when alloyed with other metals. It may be prepared by reduction of the oxide with carbon, but the temperature necessary for the reduction is so high (1105°C., Greenwood, Chem. Soc. Trans. 1908, 1491) that it is only obtained with difficulty in ordinary furnaces. The original method of preparation described by John (Gehlen's Jour. fur Chem. Phys. 3, 452) consisted in making an intimate mixture of finely divided manganous oxide and carbon by mixing with oil and heating, and exposing it to as high a temperature as possible in a crucible lined with charcoal. The impure manganese so obtained was purified by fusing under salt and nitre.

Brunner (Annalen, 102, 330) prepared the metal by heating a mixture of sodium and manganese chloride or fluoride in a blast furnace for 15 minutes. It may also be obtained by the reduction of the chloride by magnesium.

Deville obtained the metal by the reduction of the pure red oxide Mn_3O_4 by means of sugar charcoal present in insufficient quantity to reduce the whole (Ann. Chim. Phys. 1856, 46, 182).

Valenciennes (Compt. rend. 70, 907) produced it by reduction of the pure oxide with carbon in a magnesia-lined crucible as a hard and brittle mass, quickly oxidised by exposure to air.

Oxides of manganese are reduced to the protoxide but not to metal by ignition in hydrogen. Hugo Tamm (Chem. News, 26, 111) recommends the following process for the preparation on the large scale. Two fluxes are prepared. (1) A fusible 'white' flux of ground glass (free from lead) 63, quicklime 18½, and fluorspar 18½. (2) Flux No. 1 34 parts, lampblack 5½, native manganese dioxide of good quality 60½.

The crucibles used should be very refractory, lined with a mixture of 3 parts plumbago and 1 part fireclay, made into a paste with water. This casing resists the action of the flux for a considerable time. In such a crucible flux No. 2 is ignited at the highest temperature of a wind furnace with the production of 17½ parts of 'Cort manganese' and a green slag saturated with manganous oxide. Of this slag 635 parts are thoroughly mixed with 91 parts of lampblack (charcoal cannot be used), and then with 1000 parts of rich manganese ore. The whole is made into a paste with oil, pressed into the crucible, covered with a piece of wood to prevent oxidation, and luted down, leaving an aperture for the escape of gases.

The crucible is next heated in a blast furnace, at first gently, until fumes cease to escape, and finally to whiteness, for several hours. On cooling, the manganese is found as a coherent mass. The green slag may be used several times with the addition of a little white flux to increase the fluidity, provided too much gangue be not present in the ore.

Operating with an ore containing 79·5 p.c. manganese dioxide, 6·5 p.c. ferric oxide, and 10·5 p.c. gangue, the manganese obtained showed the following composition: Mn 96·9, Fe 1·05, Al 0·10, Ca 0·05, P 0·05, S 0·05, Si 0·85, C 0·95. This metal, when fused with one-eighth part of manganous carbonate, contained Mn 99·91, Fe 0·05, Si 0·015, C 0·025.

The metal is now almost entirely prepared either by reduction by aluminium by the Goldschmidt method or by means of the electric furnace. In the latter method pure manganous oxide is intimately mixed with carbon and heated in an electric furnace, a current of 300 ampères at 60 volts giving a yield of 100–120 grams of manganese in 5 or 6 minutes, or a current of 100 ampères at 60 volts giving the same amount in 10–15 minutes. Care has to be taken to avoid prolonged heating, as the metal readily volatilises in the electric furnace, and hence considerable loss may result. As carbon readily dissolves in manganese the metal so prepared usually contains from 5 to 14 p.c. carbon, which, if the manganese is volatilised, remains as graphite. By again fusing with oxide it may be obtained almost quite free from carbon and silicon (*v.* Moissan, The Electric Furance).

The principal use of manganese in the arts is in the manufacture of steel (*q.v.*), where its alloys are employed as a deoxidiser for carburising the finished steel by means of the large percentage of carbon contained, the manganese also conferring improved qualities on the steel. Both spiegeleisen and ferromanganese are smelted in blast furnaces similar to those used for making pig-iron. More basic slags and a higher temperature are, however, employed, involving a larger consumption of fuel and shorter life for the furnace lining; consequently, the boshes are usually completely water-jacketed. Spiegeleisen is manufactured containing 10–20 p.c. of manganese and 4–5 p.c. carbon, according to the demands of the steel-maker. As a considerable proportion of manganese passes into the slag (up to 6 and 7 p.c. in spiegeleisen) allowance has to be made for this in making up the charge. Ferromanganese containing 80 p.c. manganese and more with 6 p.c. carbon is manufactured and largely used in open hearth steels.

Properties.—Pure manganese is soft and does not scratch glass; if it contains but little carbon it may be kept in open vessels. As the percentage of carbon increases it becomes more readily decomposed by the moisture in the air and small fragments exposed to the air become oxidised in 24 hours with the production of hydrogen and hydrocarbons. It appears to form a definite carbide Mn_3C, which is hard and brittle, and rapidly oxidises in air, and by moisture is decomposed according to the equation

$$Mn_3C+6H_2O=3Mn(OH)_2+CH_4+H_2$$

equal volumes of methane and hydrogen being evolved. This carbide is probably present in solid solution in the impure manganese, on which it confers its hardness (*cf.* Ruff and Gersten, Ber. 1913, 46, 400).

The metal has been obtained crystalline by distillation in the electric furnace, and as a pyrophoric powder by gentle ignition of its amalgam in a current of hydrogen (Prelinger, Monatsh. 14, 353). If the temperature of ignition is too high it is no longer pyrophoric, and although paramagnetic at ordinary temperatures becomes ferromagnetic on heating.

The metal dissolves in dilute acids, and with hot sulphuric acid liberates sulphur dioxide; when used as an anode in electrolysis it behaves normally in acid and neutral electrolytes but becomes *passive* in alkaline sulphate or phosphate baths (Müller, Zeitsch. Elektrochem. 11, 755). Its sp.gr. is about 8.

The melting-point of a 99 p.c. manganese was found by Heraeus to be 1245° (Zeitsch. Elektrochem. 1902, 8, 185). According to Tiede the melting-point of manganese is 1290°. Other authorities give 1210° to 1230°. When heated in nitrogen or ammonia a nitride is formed, possessing marked magnetic properties (Shukoff, J. Russ. Phys. Chem. Soc. 40, 457); nitrides of composition Mn_3N_2, Mn_5N_2, and Mn_7N_2 are stated to exist (Wedekind and Weit, Ber. 41, 3769). From the lowering of the freezing-point by phosphorus the value 27·5 has been calculated for the latent heat of fusion (Schemtschuschny and Efremoff, J. Russ. Phys. Chem. Soc. 39, 777). At 1000° the metal is oxidised by carbon monoxide with formation of manganous oxide and carbon (Charpy, Compt. rend. 148, 560).

Detection.—All compounds of manganese, if strongly ignited, impart an amethyst-red colour to the borax bead in the oxidising flame; the bead can be rendered colourless by careful heating in the reducing flame. When heated with soda and a little nitre on platinum foil a very small quantity of manganese produces a green colour.

A very delicate test, in the absence of chlorides, consists in heating the substance or solution with dilute nitric acid and a little lead peroxide. The manganese is thus oxidised and imparts to the solution the pink colour of permanganic acid (Crum).

Minute quantities in soils, minerals, vegetables, &c., may be detected by incinerating, heating the ash with nitric acid, evaporating to dryness, taking up with water and adding to the filtrate some 40 p.c. ammonium persulphate and a drop of a 2 p.c. solution of cobalt nitrate, when a pink colour is developed on boiling.

Tetraphenyldiaminodiphenylmethane is stated to be a very delicate test for manganese (in the absence of copper). The substance to be tested is warmed with sodium hydroxide, incinerated and the ashes moistened with acetic acid. On warming with the reagent a blue colour is developed. The same colour is also produced with lead.

Manganese may be detected in N/10000 solution of manganous salts by the red colour produced by the addition of a few drops of a N/10 solution of potassium periodate (Benedict, Amer. Chem. J. 31, 381).

It may also be detected and estimated by adding to 5 c.c. of the solution, 3 c.c. of glycerol, and 1 c.c. of a 50 p.c. solution of sodium hydroxide, and then drawing a current of air through the liquid. A fine ruby colour is developed, the intensity of which is proportional to the manganese present, so that the test may be used for colorimetric estimation (Tarugi, Gazz. chim. ital. 36, 332).

When manganese is present in its usual form, as a protosalt, sulphuretted hydrogen produces a flesh-coloured precipitate from alkaline, but not from acid or neutral solutions. If ammonium hydrogen sulphide is added to a solution made alkaline with ammonia green manganese sulphide is precipitated. If the precipitation takes place at 100°, a dense green sulphide is obtained, which can be easily collected and washed. For conditions of its formation, *see* Fischer, J. Russ. Phys. Chem. Soc. 1914, 46, 1481.

Potassium and sodium hydroxides precipitate white hydrated manganous oxide which rapidly becomes brown from absorption of oxygen. Ammonia produces the same precipitate, which is soluble in excess, especially in presence of ammonium chloride, but slowly forms a precipitate of the brown oxide.

Where the manganese exists as the acid oxide, as in manganates and permanganates, the reactions are different. Alkaline manganates produce green solutions which slowly become red on exposure to air, more rapidly on addition of an acid, from production of the permanganate. Both these compounds are rapidly reduced and rendered colourless by the addition of sulphurous acid, ferrous salts, or other reducing agent. The manganese then exists as a base and shows the usual reactions. All manganates and permanganates oxidise hydrochloric acid, especially when heated, with evolution of chlorine.

Estimation.—Manganese is usually precipitated as carbonate. To the nearly boiling solution, sodium carbonate is added drop by drop, until precipitation is complete, and the solution boiled for a few minutes and the precipitate allowed to subside. It is washed by decantation three times and finally well washed on the filter. The dried precipitate is strongly ignited in a platinum crucible and weighed as Mn_3O_4, which contains 72·05 p.c. of manganese. The ignited mass should show no alkaline reaction with test paper. The precipitate of carbonate may also be converted into, and weighed as, sulphate.

A very delicate method of estimating small quantities of manganese, as in limestones, &c., has been devised by Chatard. The process, as modified by Thorpe and Hambly (Chem. Soc. Trans. 1888, 182), is as follows: The solution should be free from chlorides, should contain between 0·004 and 0·008 gram of manganese, and should occupy about 25 c.c. To it is added 5 c.c. concentrated nitric acid, 2 or 3 grams of lead peroxide, and 10–20 c.c. dilute sulphuric acid (1 acid to 2 water), and the solution gently boiled for 4 minutes. The sides of the flask are washed down to destroy any organic matter, and the liquid boiled for half a minute longer. The lead sulphate and excess of lead peroxide are allowed to settle and the solution is at once filtered (with the aid of a filter pump if possible) through a plug of asbestos recently ignited and washed with dilute sulphuric acid. The filtrate is heated to 60° and titrated with a weak solution of ammonium oxalate, freshly standardised by a standard solution of permanganate. It may also be titrated if desired with sodium arsenite, or hydrogen peroxide.

The separation from other metals is not difficult. From the alkaline earths it may be separated by addition of hydrated ammonium sulphide to the nearly neutral solution; the sulphide so precipitated is washed well, redissolved in hydrochloric acid, and precipitated as above with sodium carbonate.

From iron, chromium, uranium, and aluminium, it may be separated by digesting the dilute solution with freshly precipitated barium carbonate. These metals are thus deposited as hydroxides. The barium is removed from the solution by the addition of sulphuric acid, and the manganese precipitated as usual.

When manganese occurs together with a large proportion of iron, as in iron ores, iron, steel, &c., the following separation is useful. The nearly boiling solution of the substance in hydrochloric acid or *aqua regia*, which must be absolutely free from organic matter, is treated with ammonia, with constant stirring, until it becomes much darkened; weaker ammonia is then cautiously added until the liquid has become of a mahogany colour, but still without any permanent precipitate. A hot solution of ammonium acetate is then added. The precipitate of basic ferric acetate should be brick-red; if it be dark red, more ammonium acetate must be added. The solution is boiled for a few minutes only, and the granular precipitate filtered through a large filter paper. The filter with the precipitate is replaced in the beaker which still contains the remaining portions of the precipitate and is redissolved in hydrochloric acid, reprecipitated as before and filtered into the beaker containing the first filtrate. In this way the small portion of manganese contained in the first iron precipitate is separated. A portion of the second ferric acetate precipitate should, in important cases, be boiled with lead peroxide and nitric acid, when, if a trace of manganese be present, the liquid will acquire a pink colour.

The liquid containing the manganese may be concentrated by evaporation, filtered if necessary, and cooled. Sufficient bromine is added, with frequent shaking, to render it brown, and the whole rendered alkaline by ammonia. The manganese is thus precipitated as black hydrated peroxide.

The liquid is heated to boiling, filtered, and the precipitate washed and ignited as usual to Mn_3O_4. If a trace of organic matter be present in the solution, a portion of the iron will not be precipitated as acetate and will come down with the manganese. If this is the case the ignited oxide is redissolved and the iron precipitated as acetate, ignited, and weighed as Fe_2O_3 and its weight deducted from that of the manganese oxide obtained In ores containing lime a second precipitation of the manganese is necessary and where present cobalt and barium are usually carried down in small amounts and should be looked for after weighing the precipitate

A convenient method for the volumetric determination of manganese in ores or alloys is due to Volhard, many modifications of which have been described. The method is based on the fact that manganese salts in the presence of zinc oxide are quantitatively oxidised to zinc manganite by means of potassium permanganate ($3MnO+Mn_2O_7$ $5MnO_2$). The modification of Fischer (Zeitsch. anal. Chem. 1909, 48, 751; cf. Cahen & Little, Analyst, 1911, 36, 52) is as follows. One gram of the ore or alloy is dissolved in *aqua regia*, and the solution evaporated nearly to dryness with excess of hydrochloric acid. The residue is dissolved in 300 c c of water, mixed with a sufficiency of an emulsion of zinc oxide and made up to 1 litre. 100 c.c. of the clear solution are diluted to 500 c.c. and heated to boiling after adding 10 grms. of zinc sulphate. One gram of freshly ignited zinc oxide is added, and the liquid titrated with N/10 permanganate, boiling and shaking frequently until the supernatant liquid is red; 1 c c. of pure glacial acetic acid is then added, when the red colour disappears, and the titration is slowly finished with permanganate in the hot but not boiling liquid.

The value of pyrolusite in generating chlorine is related to its content of available oxygen, and this may readily be ascertained as follows: The well-mixed sample is ground so as to pass through a 200-mesh sieve, and dried at 105° to constant weight. 0·5 gram heated with 50 c.c. of standard ferrous sulphate solution (90 grams in 200 c.c. sulphuric acid of sp.gr 1 84, and 900 c.c. of water) until dissolved, the solution diluted to about 150 c c. and the excess of ferrous iron titrated with standard permanganate solution.

Solutions of manganous sulphate are completely precipitated as manganese dioxide, which may be subsequently estimated, when boiled with excess of ammonium persulphate. Sodium bismuthate in cold nitric acid solution oxidises manganous salts to permanganate, which may then be titrated (*v.* ANALYSIS).

Alloys.—**Iron** alloys with manganese in all proportions (*see* IRON).

Copper and **manganese** yield a continuous freezing-point curve with a minimum of 866° at 65 p.c. copper. The form of the curve and the microscopic examination of the alloys indicate that a continuous series of mixed crystals exists, and that no compounds are formed. The alloys are only homogeneous if heated for some time below the melting-point. In appearance the alloys resemble bronzes, and are generally hard and malleable. A bronze—known as 'manganese bronze'—is made by adding a copper manganese alloy to the molten bronze and usually contains from 1 to 4 p.c. manganese and from 80 to 90 p.c. copper. It forms a useful, workable alloy, possessing very great tenacity, and is used for stay bolts on some of the Continental railways. Alloys resembling German silver are also obtained from copper, zinc, and manganese.

Brunck describes an alloy with **aluminium** of composition Mn_3Al_7, which forms in white crystals soluble in hydrochloric acid (Ber. 25, 777). According to Hindricks (Zeitsch. anorg. Chem. 59, 414) two compounds exist, Mn_3Al and $MnAl_3$, both of which form mixed crystals. Alloys containing between 57 and 86 p.c. aluminium separate into two liquid layers.

Alloys with **Boron** may be produced in the electric furnace and exhibit magnetic properties due to the compound MnB. A second compound MnB_2 probably exists, but is not magnetic (Jassoneix, Compt. rend. 142, 1336).

Antimonides may be produced by the 'thermit' method By removal of excess of manganese by means of dilute acid and of antimony by chlorine, alloys regarded as MnSb and $MnSb_2$ have been obtained. Both are magnetic (Wedekind, Zeitsch. physikal. Chem. 66, 614).

With **Tungsten** alloys containing from 12 to 60 p.c. tungsten have been obtained by the 'thermit' method as hard, brittle, steel-grey ingots, from which dilute acids dissolve the manganese.

By the same method hard brittle homogeneous alloys containing from 12 to 29·6 p.c. **molybdenum** are obtained (Arrivant, Compt. rend. 143, 464, 94).

Nickel and manganese give a continuous freezing-point curve with a minimum of 1030° at 56 p.c. manganese. The addition of manganese decreases the magnetic susceptibility of nickel.

Manganese and **cobalt** form a continuous series of solid solutions, the freezing-point curve passing through a flat minimum at about 30 p.c. cobalt, and 1150°. The crystals obtained are not homogeneous, but become more nearly so after annealing in magnesia at 1000° for five hours.

Manganese and **zinc**, according to Parravano (Gazz. chim. ital. 45, 1, 1), form two alloys $MnZn_7$ and $MnZn_3$ which are hard and brittle.

With **silver** between 30 and 90 p.c. manganese, two liquids are formed, and no solid solutions (Hindricks).

With **tin** compounds $SnMn_3$ and SnMn are indicated by potential measurements. Alloys with below 40 atomic p.c. Mn are white and soft, above they become hard and brittle (Puschin, J. Russ. Phys. Chem. Soc. 38, 869).

Silicides are obtainable in the electric furnace, compounds Mn_2Si, $MnSi$, and $MnSi_2$ having been described. Of these the first forms lustrous prisms, which scratch glass, and the second can scratch topaz; the sp.grs. are 6·4, 5·9, and 5·2. The existence of these compounds is also indicated by the MnSi freezing-point curve (Doerinckel, Zeitsch. anorg. Chem. 50, 117). Gin describes also a compound Mn_3Si_2 (Compt. rend. 143, 1229).

Phosphides are obtained by heating manganous chloride and phosphorus in a current of hydrogen. Compounds Mn_6P_2 and Mn_3P_2 are described, both of them magnetic. The latter is probably, however, an eutectic mixture (Schemschuschzy and Efremoff, *l.c., supra.* Hilbert and Dieckmann (Ber. 44, 2831) have prepared the phosphide MnP as a black powder. On heating it loses its magnetic properties at 18° and regains them on cooling at 26°.

Manganese arsenides. Arsenic combines with manganese at 200° with incandescence. The arsenide Mn_2As (stable at high temperature) is grey and non-magnetic. At 700°-800° in a current of hydrogen the arsenide obtained has the composition Mn_3As_2 and is highly magnetic. The highest arsenide MnAs is stable only between 400° and 450°, and may also be obtained by the action of arsenic chloride on manganese, combination taking place with incandescence at 500°. It is highly magnetic (Arrivant, 7th Inter. Congr. App. Chem.) Hilbert and Dieckmann (Ber. 44, 2378) find that the best way of preparing pure arsenides is to heat the finely powdered metal with the vapour of arsenic under pressure. The materials are introduced into a bomb-tube of Jena glass and heated for several hours at 700°-750°. MnAs could only be obtained pure by using manganese prepared from the amalgam. It is a greyish-black powder D 6·2. The freezing-point curve of a manganese arsenide and manganese indicate the existence of three arsenides, Mn_2As, MnAs, Mn_3As_2 (Metallurgie, 8, 739). MnAs loses its magnetic properties on heating at 40° and regains them on cooling at 45°.

Manganese carbides. Trimanganese carbide was prepared by Troost and Hautefeuille and re-examined by Moissan, who obtained it by heating a mixture of trimanganese tetroxide with one quarter its weight of sugar carbon, in a carbon tube closed at one end, in an electric furnace with a current of 350 amperes and 50 volts. The reaction is complete in a few minutes; sp.gr. at 17° 6·89. Mn_3+C(diamond) $=Mn_3C$ develops +10·4 cal. $Mn_3C+3O_2=Mn_3O_4+CO_2$ develops +412·4 cal. (Le Chatelier). Water decomposes Mn_3C with evolution of methane and hydrogen in equal volumes; dilute acids attack it with formation of liquid hydrocarbons. Ruff and Borman (Zeitsch. anorg. Chem. 1914, 88, 365) have investigated the solubility of carbon in manganese in the carbon-resistance vacuum furnace, using a thermo-couple or Wanner pyrometer for measuring the temperatures. The solubility increases from 1360° to 1525°, the b.p. of the solution under 30 mm. pressure. At the latter temperature manganese saturated with carbon contains 7·12 p.c., and the vapour 1·94 p.c., carbon. Pure manganese boils at 1510°. The whole of the carbon in rapidly cooled alloys is in the combined state. The residue, after distilling the manganese, contains graphite. A carbide richer in carbon than Mn_3C is indicated. Ruff and Gersten also prepared the trimangano carbide in a similar furnace by heating a mixture of manganese and carbon at 1600° for 20 minutes under 20 mm. pressure. The manganese used was prepared by the thermit process, and had the composition Mn 98·68, Fe 0·43, Al 0·55, Insoluble 0·25, m.p. 1239° 1242°. The regulus obtained contained nests of crystals which, after separating admixed carbon by acetylene tetrabromide, were found to have the composition corresponding to Mn_3C. Molecular heat of formation from manganese and graphite 12·9±2·14 cal. (Le Chatelier, value 9·34 cal.) (Ber. 46, 400). Both carbides of iron and manganese are soft, so that the hardness of alloys cannot be due to their existence as such, but is probably due to their solid solutions. When finely powdered manganese is treated with methane or with a mixture of methane and hydrogen at 600°-900°, carbides are formed. In pure methane, carbides containing over 20 p.c. carbon are obtained. When carbides containing 8 p.c. or less of carbon are treated with dilute acids, nearly all the carbon is evolved as methane, very little ethylene and no acetylene being formed; with more than 8 p.c. carbon fatty substances and spongy carbon is produced. Manganese carbides therefore are not simple derivatives of hydrocarbons like those of calcium and aluminium (Ber. 1913, 46, 3429).

Manganese oxides. The compounds of manganese with oxygen are numerous. The lower or manganous oxide MnO is powerfully basic; the sequioxide Mn_2O_3 is less basic, the tetroxide Mn_3O_4 and the dioxide MnO_2 are practically neutral; the dioxide occasionally reacts as a basic oxide, but at other times as an acidic oxide forming *manganites* of the type M_2MnO_3, *i.e.* it belongs to the class of amphoteric oxides. The higher oxides, however, MnO_3 and Mn_2O_7, have decided acid-forming properties and produce well-marked series of salts.

Manganous oxide MnO is prepared by ignition of any other manganese oxide, or of the carbonate, in a current of hydrogen. It is of an olive-green colour and absorbs oxygen from the air with formation of a brown oxide. Heated in sulphur dioxide it is ultimately converted into manganous sulphate. In solution in acids it forms manganous salts.

Manganese sesquioxide Mn_2O_3 occurs in nature as *braunite* in brownish-black, anhydrous, acute octahedra frequently containing silica. In the hydrated form it occurs as *manganite* in brilliant, black or steel-grey, rhombic prisms.

It may be prepared hydrated, by passing chlorine, not to saturation, through water in which manganous carbonate is suspended, and removing the excess of carbonate by dilute nitric acid. It is slowly acted on by dilute acids yielding either manganic salts of tervalent manganese, isomorphous with the salts of aluminium and ferric iron, or a mixture of manganous salts and manganese dioxide. The colour of the amethyst is attributed to the presence of this oxide.

Manganese tetroxide. Red oxide of manganese Mn_3O_4 occurs as *hausmannite* in brownish-black octahedra, and in massive forms. It is produced by heating any oxide of manganese in the air. By the action of acids it yields a mixture of manganous and manganic salts or a manganous salt and manganese dioxide. It was formerly used as a pigment under the name of *manganese brown.*

Manganese dioxide. Peroxide or black oxide of manganese, frequently known as 'manganese,' MnO_2.

This important oxide occurs as *pyrolusite* in very pure iron-black or steel-grey, rectangular rhombic prisms of sp.gr. 4·8–5, and frequently massive or reniform, in radiating fibrous masses, usually brittle. Its hardness varies within wide limits, and it seldom occurs pure, but usually associated with other manganese ores.

A hydrated variety occurs largely as *psilomelane* in amorphous, massive, stalactitic, and frequently in botryoidal masses, but never in crystals. Its composition is very variable. It is usually found in the same localities as pyrolusite, frequently in alternate layers with that mineral. *Varvicite* and *newkirkite* are also hydrated varieties of pyrolusite.

Wad is an important earthy variety produced by the decomposition of other manganese minerals. It occurs, generally, in low-lying districts, in amorphous, earthy, dull black or brownish pieces of very variable composition and hardness. It frequently contains oxide of cobalt; one variety known as *asbolane* or *earthy cobalt* sometimes contains as much as 32 p.c. of cobalt. Another variety, *lampadite*, contains 18 p.c of copper oxide. In addition to its employment as a chlorine producer, wad is used as an 'umber' paint.

Of these oxides pyrolusite is the purest and contains the highest percentage of oxygen; it has therefore the greatest commercial value. At a red heat it evolves one-third of its oxygen, leaving the red tetroxide.

When heated with concentrated sulphuric acid, it dissolves with formation of manganous sulphate and evolution of half its oxygen. If organic matter be present the oxygen decomposes it with evolution of carbon dioxide.

Its action on hydrochloric acid is of great importance. The hydrogen of this acid is oxidised, a portion of the chlorine thus liberated combines with the manganese, while the remainder is set free;

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$$

On this account it is very largely used for the production of chlorine and of bleaching powder (*q.v.*).

Nitric acid has but slight action upon it. When finely divided, sulphur dioxide, at a low red heat, ultimately converts it into manganous sulphate. Pyrolusite is a good conductor of electricity and is strongly electronegative: it is used as the depolariser in the Leclanché battery. In the electric furnace it melts and evolves oxygen forming the monoxide. It is used in conjunction with other oxides for producing warmer shades in coloured glass and to destroy the injurious tint produced in colourless glass and white enamels by the presence of ferrous compounds. The oxygen converts the greenish salt into the nearly colourless ferric salt, whilst the slight pink tint imparted by the manganese still further counteracts the bluish colour. It seems probable that the effect is due principally to the latter cause, as red lead and other oxidising agents have not this decolorising power.

Pyrolusite is also used in the preparation of dark violet, black, and metallic-like enamels for pottery and enamel iron ware. It is also added to cheapen blue enamel by intensifying the colour of cobalt, to which, however, it imparts a violet tint. It has been used as a pigment under the name of *manganese black.* It is used as a *drier* for oils, *i.e.* a substance added to confer drying properties to the oils. It is one of the most powerful driers known, and is added in the proportion of about ¼ lb. to 1 cwt. of oil. The 'tackiness' of rubber is augmented by small quantities of manganese oxide.

Manganese dioxide may be prepared artificially by moderately igniting the nitrate, boiling the residue with nitric acid, washing and gently heating (Berthier). The hydrated oxide has been used for the removal of iron from aluminium sulphate.

According to Fremy (Compt. rend. 82, 1231) it forms a definite sulphate on solution in sulphuric acid, and a solution containing this under the name of manganese peroxide sulphate, produced by the electrolysis of a sulphuric acid solution of manganous sulphate is used as a mild oxidiser in aniline dye manufacture. Double salts containing $MnCl_4$ also exist.

Colloidal manganese dioxide may be obtained by the action of potassium permanganate on a solution of dextrose, lævulose or galactose in dilute solution of alkali hydroxide: it first passes into a viscous or gel stage, and subsequently into a limpid, colloidal solution. The colloid is best formed at low temperatures, and the concentrated colloid is readily coagulated on warming (Witzemann, J. Amer. Chem. Soc. 1915, 37, 1079; *cf.* Bredig and Marck, Chem. Zentr. 1911, 1, 1190). A convenient method of preparing it consists in adding strong ammonia solution at the rate of one drop every 3 minutes to a boiling N/20 solution of potassium permanganate until it has become deep coffee-coloured and has lost the characteristic colour of permanganate (Guy, J. Phys. Chem. 1921, 25, 415). Chronic manganese poisoning has been observed to occur in workers handling or grinding manganese dioxide, or working in dust containing manganese as oxides or silicates (Chem. Abstr. Amer. Chem. Soc. 1919, 13, 3243).

Manganese trioxide. Franke (J. pr. chem. 1887, 14) has described a trioxide MnO_3; its existence has been confirmed by Thorpe and Hambly (Chem Soc. Trans. 1888, 177). This oxide appears to form a sulphate $(MnO_3)_2SO_4$

Manganese heptoxide Mn_2O_7 is a highly hygroscopic, non-volatile, reddish-brown liquid, which gradually decomposes on exposure to the air. Its composition was determined by Aschoff (Pogg. Ann. 3, 217). These two oxides are of interest, as they form the acid radicles of manganates and permanganates; thus, $MnO_3{\cdot}K_2O$, $Mn_2O_7{\cdot}K_2O$.

SALTS OF MANGANESE.

Of the salts corresponding to these various oxides, only two series are of practical importance, manganous salts, corresponding to the monoxide, and manganates and permanganates, in which manganese acts as an acid corresponding to the tri- and hept-oxides.

Manganous chloride $MnCl_2$ is produced by the action of chlorine gas on metallic manganese, or of hydrochloric acid gas on the heated carbonate. In solution, it is obtained by dissolving the oxide or carbonate in hydrochloric acid.

On the large scale it is usually produced from the residual solutions from the chlorine manufactures. This is first evaporated to remove excess of hydrochloric acid, and one-fourth of the solution is removed and precipitated by sodium carbonate. The precipitate, which contains manganous carbonate and ferric hydrate, is washed and boiled with the remainder of the solution. The iron in solution is thus precipitated as hydrate, being replaced by an equivalent quantity of manganese from the carbonate. Copper, if present, is precipitated by the addition of sulphuretted hydrogen, leaving in solution manganese, and usually calcium and other alkaline earthy metals. Cobalt and nickel may be removed by the addition of freshly precipitated manganous sulphide, as long as it becomes darkened; those metals are then precipitated as sulphides.

The manganese is precipitated by means of ammonium sulphide, washed, dissolved in hydrochloric acid, evaporated, and crystallised.

It may be obtained pure by evaporating the crude solution of the ore in acid to dryness, igniting gently in a crucible, exhausting the residue with water, concentrating and crystallising. It forms pink deliquescent crystals, containing 4 molecules of water, soluble in two-thirds their weight of water at 60°, soluble in alcohol.

In commerce it usually occurs as a rose-red, very deliquescent mass, obtained by evaporating the solution to dryness. It is used for dyeing cotton manganese-brown or -bronze. The fabric is soaked in a solution of the salt and then passed through a caustic alkali, whereby manganous hydroxide is precipitated in the fibre and by subsequent atmospheric oxidation becomes brown. The material thus treated may also be used for the subsequent dyeing by aniline black. The presence of over 1 p.c. calcium chloride in the salt renders it practically useless for calico-printing and dyeing.

Manganous sulphate $MnSO_4$ may be prepared by dissolving the carbonate or oxide in sulphuric acid. On the large scale it is usually obtained from the black oxide. This is heated with about one-tenth part of powdered coal, and is thus reduced to the monoxide. The mass is dissolved in sulphuric acid, evaporated, gently heated to decompose the ferrous sulphate, and the manganous sulphate dissolved out by water. By another process the peroxide is first digested with dilute sulphuric acid to remove carbonates, and made into a paste with strong sulphuric acid, heated until the evolution of oxygen has ceased, and then to strong redness, cooled, digested in water, and the solution evaporated and crystallised. If iron be still present, it may be removed as in the case of the chloride by boiling with manganous carbonate. Manganous sulphate forms pink crystals with 7 mols. of water very soluble in water, insoluble in absolute alcohol. It is used in calico-printing. It is also used as a drier for pale oils or for conversion into the oxalate or borate which are also used for the same purpose. For other hydrates *see* Forcrand, Compt. rend 1914, 158, 1760; *ibid.* 159, 12. All manganous salts are strong reducing agents.

Manganese borate, used as a drier, is a salt of a faint pink colour, prepared by adding a solution of borax to one of a manganous salt, washing and drying the powder so obtained.

Manganese oxalate, also used as a drier, is prepared by precipitation of a manganese salt by a soluble oxalate, or by the action of oxalic acid on manganese hydroxide or carbonate. *Manganese linoleate* is also used for the same purpose, and prepared by addition of linseed oil-soap to manganous chloride.

Manganese sulphide Mn_5 occurs in nature as *alabandite*, an almost black mineral (streak green) crystallising in the cubic system, sp.gr 4·00 (artificial variety, 4·03), m.p. 1620 (Rohl). It is precipitated from its solutions by alkaline sulphides in either the rose-coloured or green form (*see under* DETECTION). Manganese sulphide is of great importance in the manufacture of steel. The addition of manganese to steel containing sulphur prevents red shortness, the latter effect being due to the solubility of iron sulphide in liquid steel, whereas the addition of manganese precipitates the sulphur as insoluble manganese sulphide.

Potassium manganate K_2MnO_4. This compound is produced when equal weights of finely powdered manganese dioxide and caustic potash are fused together, a sesquioxide of manganese being produced at the same time. By the addition of potassium nitrate or by performing the ignition in a flat vessel, a portion of this oxide is re-oxidised, and increases the yield of manganate.

It dissolves in water, forming a fine green solution, which, on evaporation *in vacuô*, produces green crystals isomorphous with potassium sulphate and chromate. The solution, especially if dilute, when exposed to the air becomes converted into the permanganate with precipitation of hydrated manganese dioxide; the liquid passes through various shades from green to pink, whence its name of 'mineral chameleon.' In presence of excess of alkali this change does not take place. On the addition of free acid, especially sulphuric acid, the change is immediate, the alkali and manganese, instead of being liberated as hydrates, being at once converted into sulphates, and thus losing their tendency to reproduce the manganate. Potassium manganate is a powerful oxidising agent. Its general action in this respect resembles that of the permanganate.

Sodium manganate Na_2MnO_4 is largely manufactured for disinfecting purposes on account of its greater cheapness.

Barium manganate $BaMnO_4$ is formed by heating manganese dioxide with barium hydroxide or carbonate with addition of barium nitrate. Is an emerald-green microcrystalline powder, insoluble in water. Sp.gr. 4·85. Has been used as a pigment in place of the more poisonous Scheele's Green.

Potassium permanganate $KMnO_4$. This salt may be prepared by the addition of 10 parts of potash dissolved in the minimum of water to a mixture of 8 parts manganese dioxide and 7 parts potassium chlorate. The solution is evaporated to dryness, finely powdered, and ignited at a dull red heat for about 1 hour, until the chlorate has become decomposed. The mass is boiled with water, decanted, evaporated rapidly to a small bulk until crystals form on its surface, decanted from the precipitate which has fallen, and allowed to crystallise; 1 part of permanganate is produced from 3 parts of the oxide (Gregory, J. Pharm. Chim. 21, 312).

It is, however, usually prepared by the action of an acid on the manganate.

According to Stadeler (J. pr Chem. [i] 103, 107), 90 p.c. of the oxide may be converted into permanganate by first preparing the manganate and converting it into permanganate by the addition of chlorine instead of acid

$$2K_2MnO_4 + Cl_2 = 2KCl + 2KMnO_4$$

The solution is evaporated and the permanganate crystallised, leaving the potassium chloride in solution.

Tessié du Mothay and Maréchal prepare it by addition of magnesium sulphate to the manganate, according to the equation

$$3K_2MnO_4 + 2MgSO_4 + 2H_2O$$
$$= 2KMnO_4 + 2K_2SO_4 + 2Mg(HO)_2 + MnO_2$$

It may also be prepared electrolytically by passing a current through a solution of the hydroxide using a ferromanganese anode (White, J. Phys. Chem. 10, 592; Wilson, Horsch and Youtz, J. Ind. Eng Chem. 1921, 13, 763).

On the large scale powdered pyrolusite (96 kilos. of 50 p.c. ore) is placed in an iron basin, 95 litres of potash lye (sp.gr. 1·5) are slowly added with stirring, and the mixture is heated till the mass is completely dry. The stirring is stopped from time to time, and any large lumps are broken down with a wooden hammer (the formation of these lumps is an indication of the favourable working of the process). The operation needs 100 kilos. of coal, lasts 12–14 hours, and results usually in the decomposition of 60–65 p.c. of a natural ore, or 40–45 p.c. of 'regenerated ore' (*see* below). The product is ground in a ball mill, and is then transferred to pressure-heaters, *i.e.* double-walled, cast-iron basins with the interspace filled with lead. These are heated from below to 260°–270°; they are provided with stirrers and with a circular pipe welded on to the lid, through holes in which, corresponding with holes in the lid, compressed air is admitted, preferably heated also to 260°–270°. This operation, which increases the yield of manganate, lasts 10–12 hours for 300 kilos. of substance. The mass is now dissolved in the filtered liquors and wash-waters from the electrolysis and crystallisation of a previous batch, at a temperature of about 40°, in a vessel provided with stirrers; potassium manganate and hydroxide go into solution, and a certain amount of manganese peroxide (known as 'regenerated ore') is formed. This is separated by sedimentation, the liquid drawn off through filters, and the deposit washed. The clear solution (sp.gr. about 1·4) is electrolysed in cylindrical iron vessels with conical bottoms fitted with iron stopcocks, nickel anodes, and iron cathodes, which are fastened by glass and cement to the bottom of the vessel, being used. Each cell holds 960 litres, and is filled to within 20 cm. of the rim. The liquor is preferably warmed to about 30°C., and a current of 30–40 ampères per sq. dcm. used, the voltage being 2·5–2·7. The operation continues from 10–11 hours, and the end is judged by the red colour of a sample on a glass rod. The whole contents, including any crystals, are now poured into cooling cylinders, and cooled—in winter by cold water, in summer by water and ice; the salt is separated from the mother liquor centrifugally, and washed in the centrifuge. The salt is then dried *in vacuô*, and carefully passed through a small ball-mill to break up portions that have caked in drying. In this way a salt of 99 p.c. purity is obtained. When the mother liquor (which goes into the process again) has accumulated as much as 10 p.c. of carbonate, it must be causticised; it is concentrated to sp.gr. 1·32, any separated permanganate or manganese peroxide removed, the liquor diluted to sp.gr. 1·1, causticised with lime, and again concentrated to sp.gr. 1·5 (Schutz, Zeitsch. angew. Chem. 1911, 24, 1628; J. Soc. Chem. Ind 1911, 30, 1157).

According to Deselabissac (Dingl. poly. J. 201, 58), the following methods are used for the preparation of sodium manganate and permanganate on the large scale. (1) 500 parts of soda lye (45°B.) are evaporated with 100 parts potassium chlorate mixed with 180 parts of the finely powdered oxide, and ignited in iron pots until quietly fused, cooled, with constant stirring, again heated to redness, cooled, and extracted with water. (2) 12 parts of caustic soda, dissolved in 58 parts of water are heated with 12 parts potassium chlorate and 18 parts manganese dioxide, until it begins to crumble; the heat is then increased to redness, and the mass, after cooling, is extracted with 200–220 parts of water. (3) To a fused mixture of 10 parts caustic soda and 1 part nitre are added 6 parts strongly heated manganese dioxide; the cooled mass is ladled out and extracted as before.

Condy's fluid consists chiefly of a mixture of sodium manganate and permanganate (*v. infra*). For its preparation 30 cwt. of soda ash are converted into caustic soda by lime; they are then mixed with 7 cwt. manganese dioxide, and ignited in a shallow vessel at a dull red heat for about 48 hours. The mass is treated with water, decanted, and the solution evaporated to the required concentration. When the product is required to consist only of permanganate the solution is treated with sulphuric acid, and evaporated until crystals of sodium sulphate separate. Sodium permanganate is, however, much more difficult to purify by crystallisation than the potassium salt (*v.* Hofmann, Reports on Chem. Processes at the Exhibition of 1862, 109)

Potassium permanganate forms fine dark purple prismatic crystals of greenish metallic lustre, soluble in 19 parts of water at 15°. Sp.gr. 2·7. When heated they decompose, at 200–240°

$$10KMnO_4 = 3K_2MnO_4 + 2K_2MnO_3 + 5MnO_2 + 6O_2$$

Heated in hydrogen they ignite and leave a green mass containing manganese monoxide and potash.

It is a powerful oxidising agent; each molecule contains five atoms of 'available' oxygen, *i.e.* more than any other salt. It is largely used as a disinfectant.

When triturated with sulphur or phosphorus it detonates; when mixed with carbonaceous matters and many other reducing agents, and heated, it burns. Mixtures containing permanganates and organic substances are very liable to spontaneous decomposition.

The crystals oxidise strong hydrochloric acid in the cold, with evolution of chlorine; in solution the same effect is produced on heating.

A solution of the salt is rapidly reduced by sulphurous acid, ferrous salts, and most other reducing agents; less rapidly by organic matter. The solution is therefore used as a test for such substances, and to estimate their amount.

Solutions of the salt can only be filtered through asbestos or glass wool, as they quickly destroy filter-paper.

Zinc, iron, lead, mercury, and many other metals are oxidised more or less rapidly by the solution. Pure potash has no action on permanganate, even when heated, but in presence of organic matter the permanganate is rapidly reduced to the green manganate.

On mixing concentrated solutions of this salt and of silver nitrate, a red crystalline precipitate of **Silver Permanganate** $Ag_2Mn_2O_8$ is produced. It may be used for the preparation of other permanganates. On mixing with a solution of barium chloride, silver chloride is precipitated, and **Barium Permanganate** remains in solution, from which *permanganic acid* may be produced by the addition of dilute sulphuric as long as a precipitate falls. On evaporating the solution the acid is obtained as a brown, crystalline, very soluble mass, easily decomposed by heat.

Sodium permanganate $Na_2Mn_2O_8$ resembles in its properties the potassium salt (*v. Sodium Manganate*).

Aluminium permanganate. Condy (Eng. Pat. 1884, 10015) patented a method of preparing this salt for disinfecting purposes. It is said to give up five-sevenths of its total oxygen to reducing agents. The alumina present would also assist in the precipitation of impurities in water, &c. To 1000 parts of a solution of aluminium sulphate, containing one-third its weight of the sulphate, is added 53 parts of potassium permanganate, which is dissolved by the aid of heat. On cooling, potassium alum crystallises out, and the decanted solution, which contains the whole of the permanganate and a considerable amount of aluminium sulphate, is ready for use.

MANGANESE BRONZE *v.* MANGANESE; TIN.

MANGANESE-SPAR *v.* RHODONITE; RHODOCHROSITE; and MANGANESE.

MANGANIN *v.* NICKEL.

MANGANITE. A manganese-ore consisting of hydrated sesquioxide $Mn_2O_3{\cdot}H_2O$ or $MnO(OH)$. It occurs as well-developed orthorhombic crystals of prismatic habit and as columnar masses. These possess three perfect cleavages in the direction of the length of the prism, namely, one parallel to the brachypinacoid and two parallel to the unit rhombic prism. The colour is dark steel-grey, with a sub-metallic lustre, and the streak is brownish-black; sp.gr. 4·3, hardness 4. Good crystals are found, often in association with barytes, at Ilmenau in Thuringia, Ilfeld in the Harz, Granam in Aberdeenshire, Bridgeville in Pictou Co., Nova Scotia, &c. The mineral readily alters to pyrolusite (MnO_2), owing to loss of water and oxidation, the material becoming softer and heavier and with a blacker streak. Pseudomorphs of pyrolusite after manganite are of common occurrence. Manganite occurs together with the other black oxides of manganese (pyrolusite, psilomelane, &c.), but as an ore of manganese it is less abundant than these. L. J. S.

MANGANOSITE. Manganous oxide, MnO, crystallised in the cubic system, and isomorphous with periclase (MgO). Small amounts of magnesia, lime, and ferrous oxide are also present as isomorphous replacements. The small grains and octahedral or rhombic-dodecahedral crystals have a cubic cleavage, and are transparent with an emerald-green colour, but become black on exposure. The material has a strong selective absorption, the spectrum of transmitted light consisting of a narrow red band and a rather wider green band. The refractive index for these two colours is 2·16 and 2·19 respectively. Sp.gr. 5·18–5·36, H. 5–6. The mineral dissolves with difficulty in strong nitric acid to a colourless solution. It has been found with manganese ores at Langban in Sweden, with magnetite at Nordmark in Sweden, and with franklinite and zincite at Franklin in New Jersey. Possibly it is of more frequent occurrence in manganese ores than has hitherto been recognised. L. J. S.

MANGEL-WURZEL or **MANGOLDS.** *Beta vulgaris* (Linn.). A plant largely grown as a farm crop, the root being used as a winter food for cattle and sheep. It is a variety of the garden beet-root or of the sugar-beet. Many varieties are known, differing in size, shape, and colour. Average composition—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Large roots .	89·5	1·3	0·1	6·7	1·0	1·4
Medium ..	88·0	1·2	0·1	8·7	0·9	1·1
Small .. .	86·5	1·1	0·1	10·6	0·8	0·9

Large roots of any variety are more watery, richer in nitrogenous substances and crude fibre than small ones; they are not so valuable for feeding purposes nor do they keep so well. When first harvested, mangolds are not suitable for food, especially for sheep, but after keeping a few weeks they form a valuable addition to the dry, winter food of all farm animals. The beneficial effect of storage appears to be the conversion of nitric nitrogen into amides (Wood, J. R. Agric. Soc. 1898).

The nitrogenous constituents of mangolds include much non-proteid material, in which betaine, asparagine, glutamine, nitric acid, and ammonia are the most important. Of the total nitrogen in the root, about 48 p.c. exists as true proteid, from 1 to 6 p.c. as betaine, about 4 p.c. as ammonia, and from 10 to 15 p.c. as nitric acid; the proportions, however, are subject to great variations.

The nitrogen-free extract consists largely of sugar, but there are also present oxalic acid, citric acid, pectins, and pentosans.

As an example of a more detailed analysis of mangolds the results obtained by Pitsch (Landw. Versuchs-Stat. 1892, 21, 471) in an analysis of the dry matter of ' Golden Tankard ' mangolds (the roots contained 86·82 p.c. water) may be quoted—

Protein	Pure proteid	Nitric acid	Fat	Sugar	Other N-free substances	Crude fibre	Ash
8·75	4·06	0·31	0·58	60·17	16·98	6·33	7·36

The ash of mangolds, according to König, contains—

Per cent of ash in dry matter	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
6·44	53·0	15·4	4·1	4·5	0·8	8·4	3·1	2·3	8·4

The leaves are sometimes used as food for cattle, but are very watery and contain oxalic acid (3 or 4 p.c. of the dry matter). They sometimes produce poisonous symptoms if used in large quantities. The addition of about 1 part of finely divided calcium carbonate to 1000 parts of leaves is found to prevent the poisonous action of the oxalic acid. Kellner gives as the average composition of the leaves—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
89·0	2·4	0·4	4·6	1·6	2·0

Mangold seeds have been examined by Devarda (Landw. Versuchs-Stat. 1897, 49, 239). They consisted of 11·55 p.c. of water and 88·45 p.c. of dry matter. The dry matter contained—

Protein	Fat	N-free extract	Crude fibre	Ash
12·84	6·08	38·41	34·01	8·38

The ash consisted of—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
22·0	8·0	16·1	[illegible]1·0	1·0	10·0	5·0	24·6	2·3

Mangolds require a deep, somewhat loamy soil, and, with abundant nitrogenous manuring, yield very heavy crops. They have a longer period of growth than turnips, and are less dependent upon phosphatic manuring. They are one of the few crops which are benefited by applications of common salt to the soil and, perhaps for this reason, grow well on land near the coasts. H. I.

MANGO. The fruit of *Mangifera indica* (Linn.), a tree of the East Indies, now grown in other tropical countries. It is eaten raw or used for the preparation of pickles and chutneys.

Prinsen-Geerligs (Chem. Zeit. 1897, 21, 719) gives the following data :—

	Mean weight in grammes	Flesh p.c.	Rind p.c.	Stone p.c.	The flesh contains Glucose	Lævulose	Sucrose
Sweet variety	200	67	3	30	0·6	2·0	9·5
Sour variety	300	75	3	22	0·0	1·9	3·6

The gum of this tree was examined by Lemeland (J. Pharm. Chim. 1904, 19, 584), who found it to consist largely of galactose and pentoses. H. I.

MANGOSTIN $C_{23}H_{24}O_6$, a crystalline substance first isolated from the skin of the mangosteen fruit by Schmid (Annalen, 1865, 93, 83). It crystallises in small, flat, pale-yellow needles, and dissolves in solutions of alkali hydroxides to form unstable salts which are decomposed by carbon dioxide. Ferric chloride gives with an alcoholic solution, a greenish-brown coloration discharged by hydrochloric acid. Oxidised by warm nitric acid or potassium permanganate with formation of oxalic acid and other products. On fusion with potassium hydroxide yields amyl alcohol, acetic, valeric, and benzoic acids. It contains two phenolic hydroxyl groups, one methoxyl group, and one or more amyl groups. *Dimethyl mangostin* $C_{25}H_{28}O_6$, m.p. 123°, obtained by shaking a solution of mangostin in dilute potassium hydroxide with methyl sulphate, forms faintly yellow slender needles (Hill, Chem. Soc. Trans. 1915, 107, 595).

MANGROVE BARK. The bark of the mangrove is exported from Mozambique, Parapat, Ibo, Pemba Bay, and other parts of East Africa, mainly to Germany, Russia, and the United States, and for use as a tanning material. It contains from 35 to 40 p.c. of tannin.

MANILA ELEMI *v.* OLEO-RESINS.

MANIOT or **MANIHOT** is the farina of *Manihot utilissima* (Pohl.), formerly known as *Jatropha Manihot* (Linn.), the plant which furnishes tapioca. Indigenous to America, but also cultivated in Africa and tropical climates generally. Maniot is occasionally imported under the name of ' Brazilian arrowroot.'

MANJAK. A form of asphaltum found in Barbados and Trinidad. It melts above 204°. The principal deposits occur in Trinidad, about 3 miles from San Fernando, as long seams between layers of clay. Boiled with oil and applied in a liquid state it affords a tough, unbreakable, rubber like protective coating, impervious to air and water. It is used in connection with rotatory drilling for oil, being employed to fill the joints of the pipes between casing-threads and drill stem heads. As a paint it efficiently protects iron and steel goods from sea-water, and is useful as a roofing material in tropical countries.

MANNA. The concrete juice of the manna-ash, *Fraxinus Ornus* (Linn.), *rotundifolia*, *F. o. angustifolia*, *F. fraxinaster oxyphylla*, *F. f. australis*, and *F. f. excelsior*. The *Ornus* trees yield the best manna, but the *Fraxinaster* the greatest quantities. Ordinary manna is procured by making incisions in the bark of the trees during the summer and allowing the sap to evaporate. Most of the manna of commerce comes from Sicily or Southern Italy. When freshly prepared, it is pleasant to the taste and is used, to some extent, as a food ; but on keeping, it acquires mild laxative properties and is used medicinally.

Manna consists largely of mannitol (*q.v.*), of which it is usually stated to contain from 50 to 70 p.c., together with some invert sugar, gum, and ash. According to Tanret (Bull. Soc. chim. 1902, 27, 947), however, it contains notable quantities of two complex sugars, which he names *manneotetrose* and *manninotriose*. His analyses show ordinary manna to contain mannitol 40–55, lævulose 2·5–3·4, dextrose 2·2–3·0, manneotetrose 12–16, manninotriose, 6–16 p.c., together with small quantities of resin and ash.

Marogna (Bull. Agric. Intell. 1915, 6, 835) gives analyses of genuine commercial samples of Sicilian manna as follows: Moisture 5–11; mannitol 33–61; reducing sugars, before hydrolysis, 10–16; after hydrolysis at 100°, 26–55. Dry distillation of manna *in vacuô* yields a dense liquid which apparently contains mannitol anhydrides, *mannide* and *mannitan*, these yielding mannitol on hydrolysis.

Mannceotetrose $C_{24}H_{42}O_{21},4H_2O$ forms monoclinic crystals, melts at 100°, and has $[\alpha]_D+150°$; it is very soluble in water, does not reduce Barreswil's solution, and is hydrolysed by acetic acid or enzymes, yielding lævulose and manninotriose; or by dilute mineral acids into 1 mol. dextrose, 1 mol. lævulose, and 2 mols. galactose.

Manninotriose $C_{18}H_{32}O_{16}$ separates from hot alcohol in spherical masses, melts at 150°, and has $[\alpha]_D+167°$. It reduces Barreswil's (Fehling's) solution, slowly ferments with yeast, and is hydrolysed by mineral acids, but not by enzymes.

Among many other vegetable exudations which go by the name of 'manna' the following may be mentioned:—

Australian manna: (*a*) from *Myoporum platycarpum* (R. Br.) contains mannitol 89·6, sugar 3·4, water 3·5, ash 1·1 p.c. (Malden, Chem. Zentr. 1894, ii. 341).

(*b*) From the leaves of *Eucalyptus dumosa* (A. Cunn.) containing sugar, inulin, starch, and gum (Anderson, quoted by König).

(*c*) From *Eucalyptus Gunnii*, var. *rubida*, contains water 9·7, ash 6·8, melitose 68·5, dextrose 20·9, sucrose 2·4, gum 3·2, insoluble 4·3 p.c. (Ebert, Chem. Zentr. 1908, ii. 1874).

Persian manna, from the leaves and thorns of the camel's thorn, *Alhagi maurorum* (Medic.) containing moisture 5·2, ash 9·4, chlorophyll and some gum 0·5, sucrose 42·0, gum 20·3, residue 32·0 p.c. (E.).

Sinai or *Tarfa manna*, exuding from punctures caused by an insect, *Coccus manniparus* (Ehrbg.), in the stems of *Tamarix gallica*, var. *mannifera*, containing chiefly sugar and dextrin. *Cedar* or *Lebanon manna*, from the branches of *Cedrus Libani* (Barrel. Ic.).

Trehala manna from the larval cocoons of a beetle, *Larinus maculatus*, living on the stems of *Echinops persicus* (Stev.), containing water 11·1, ash 2·6, trehalose 17·5, gum 27·1, tannin, starch, and residue 44·5 p.c. (Ebert, *loc. cit.*).

Manna of olives, a morbid secretion of bacterial origin caused by the attacks of insects upon olive trees, contains 52 p.c. mannitol, 7·8 p.c. reducing sugars, and 21·5 p.c. of other organic matter (Trabut, Compt. rend. 132, 225).

The term 'manna' is also loosely used for the seeds of certain cereals, *e.g.* 'Boer manna,' and 'Kaffir manna' are often employed as names for certain millets. H. I.

MANNHEIM GOLD *v.* GOLD, MANNHEIM.

MANNITOL, MANNOSE, MANNOTRIOSE *v.* CARBOHYDRATES. Mannose may be prepared from ivory nut shavings in the form of powder by treatment with a hot 1 p.c. solution of sodium hydroxide, followed by digestion of the perfectly dried residue with 75 p.c. sulphuric acid for 6 hours, the solution diluted with water boiled for 6–8 hours, and, when cold, mixed with calcium hydroxide, filtered, treated at 90° with decolorising carbon, cooled, and, after adding excess of calcium or barium carbonate, again filtered, concentrated *in vacuô* to a syrup, poured into an equal volume of alcohol of 95 p.c. alcohol, again treated with decolorising carbon and again filtered. After further concentration *in vacuô*, the almost solid mass is dissolved in warm glacial acetic acid and crystallisation assisted by seeding (Horton, J. Ind. Eng. Chem. 1921, 13, 1040; Clark, J. Biol. Chem. 1922, 51, 1).

MANQUETA or **MAQUATA.** African names of a fossil gum-resin, resembling copal gum, found in Angola, below the surface of a ferruginous hard clay or soil, at a depth of a few inches to a couple of feet, often in pieces weighing several pounds.

MANTLES, GAS *v.* GAS MANTLES.

MANURE, ARTIFICIAL *v.* FERTILISERS.

MAPÉ. A coarse starch obtained from Tahiti, derived from the fruit of *Inocarpus edulis* (Forst.).

MAPLE. The name of trees of the genus *Acer*. Some species are valued as shade and timber trees, whilst one, *A. saccharinum* (Wangenh.), affords an important source of sugar in America and Canada. This tree, which attains a height of 100 feet with a trunk of 3 or 4 feet in diameter, affords a considerable quantity of saccharine sap if tapped in the early spring. The sap varies in composition, but, on the average, contains from 2 to 3 p.c. of sucrose, small quantities of proteids, ash constituents, and vegetable acids, mainly malic acid. The flow of sap is most rapid when frosty nights are followed by warm days. The sap is received in buckets and rapidly boiled down in an open pan, the proteid matter which coagulates being removed by skimming. A deposit, often containing calcium malate and silica, forms on the pan bottom. When the syrup has attained a sufficient density it is run off and either preserved as syrup, after filtration or sedimentation, or is boiled down still further, until it solidifies to a white or brown mass of sugar on cooling.

Maple sugar and syrup are highly prized for table use in America and Canada, and are chiefly used in the locality where they are produced. They vary considerably in composition according to the method adopted in their preparation, but generally retain a characteristic 'maple' flavour.

Genuine maple sugar is distinguishable from imitations made of cane sugar by the large precipitate it yields with basic lead acetate, mainly due to the malic acid present (*see* Winton and Kreider, J. Amer. Chem. Soc. 1906, 28, 1204). For the results of an investigation into the conditions affecting the flow of sap of the sugar maple, *see* Jones, Edson and Morse (Bull. 103, Vermont, Expt. Stat. 1903). H. I.

MAQUI. The maqui is a small evergreen liliaceous shrub (*Aristotelia Macqui*, L'Hérit.), common in Chile along the course of torrents, and in shady mountainous woods. It is not cultivated, but grows wild, and the berries, which in Chile are eaten either fresh or preserved, contain a red pigment, and are exported largely to Europe for the purpose of colouring wines.

MARBLE (Fr. *Marbre*; Ger. *Marmor*). Although this term should strictly be limited to those varieties of limestone (*q.v.*) which are sufficiently compact to receive a polish, it is loosely applied in trade to a great range of ornamental stones, including many which, like serpentine and alabaster, are not even limestones. Typical marble, such as that used for statuary, has a crystallo-granular texture, resembling that of loaf-sugar, whence it is termed 'saccharoidal.' Under the microscope it commonly shows an aggregation of grains of calcite, exhibiting twin-lamellæ. The development of such a structure appears to be due to that kind of metamorphic action which Sir A. Geikie has termed *marmorosis*. That an ordinary limestone may be converted by the operation of heat and pressure into a crystalline marble is known to every field geologist, while the fact has been confirmed experimentally by Sir J. Hall (in 1805) and others. Impure limestones, when altered by metamorphic processes, are often rich in various crystallised silicates, such as garnet, idocrase, tremolite, and mica. An analysis of Carrara marble gave: $CaCO_3$ 98·77, $MgCO_3$ 0·90, SiO_2 0·16, $Al_2O_3+Fe_2O_3$ 0·08=99·91.

Of ancient marbles, the most renowned for the purposes of sculpture was the *Parian*, obtained from the isle of Paros, one of the Cyclades, in the Ægean sea. The finest kind, known as *Lychnitis*, had a peculiar sparkling grain and a warm surface, which enabled the sculptor to render the texture of skin with great effect. The old quarries have been described by R. Swan (Brit. Ass. Rep. Newcastle, 1889). The famous *Pentelic* marble, largely used in Athenian architecture in the age of Pericles, was a coarser material, adapted for bold sculpture rather than for delicate statuary. *Carrara* marble, extensively employed in Rome under the name of *Luna* marble, and used by Michael Angelo and Raphael, is a very fine-grained saccharoidal limestone, still worked with other varieties at Carrara, Massa, and Serravezza, in Tuscany.

The ancient marbles used in Italy have been studied by F. Corsi (Delle Pietre Antiche, Roma. 1833, 3rd edit., 1845) and other antiquaries. *Giallo antico* was a fine yellow marble from Numidia, while *Rosso antico* was a homogeneous red marble, probably from Greece, sometimes confounded with *Porfido rosso antico*, a hard red porphyry with white felspar crystals, from Jebel Dokhan in Egypt. *Verde antico* is a mixture of serpentine and limestone from near Atrax, on the Peneus, in Sicily, quite distinct from the *Porfido verde antico*, or Lacedæmonian stone, a felspathic porphyry from Mount Taygetus. Many marbles are known by fanciful names derived from colour, locality, or a superficial resemblance to natural objects: thus, *Bardiglio* is a grey or bluish marble with white veins, whilst *Cipollino* is a white marble with green veins of mica or talc. (On Italian marbles *v.* W. P. Jervis, I Tesori Sotterranei dell' Italia, vol. 4, Torino, 1889. For ancient marbles *v.* M. W. Porter. What Rome was Built with, Oxford, 1907; H. W. Pullen, Handbook of Ancient Roman Marbles, London, 1894.)

The marbles of the British Isles are derived mainly from the Devonian and Carboniferous formations. *Plymouth* marble occurs in the Upper Devonian, while the Great Devon limestone, of Middle Devonian age, has been worked as a marble at Babbacombe and St. Mary Church. The *Madrepore marbles* of Torquay are largely used for trivial ornaments. The Carboniferous limestone of Derbyshire has long been famous for the beauty and variety of its marbles, the best known being the *Encrinital* marbles, which owe their characteristics to the embedded remains of crinoids or 'stone lilies.' Similar encrinitic marble occurs at Dent in Yorkshire and in King's Co., Ireland. *Rosewood* marble is a beautiful brown variety from Ashford in Derbyshire. *Black* marble, such as is worked in Derbyshire, Galway, and Kilkenny, usually emits a fetid odour when struck, and loses its colour on calcination. W. N. Hartley found 1·48 p.c. of carbon and 0·01 of sulphur in the black marble of Kilkenny (Proc. R. Dub. Soc. 1887, 5, 486). The black Carboniferous limestone of Belgium and France, with small white sections of encrinites, is termed locally *Petit granit*.

Lumachella is an Italian name for any shelly marble, but is specially applied by mineralogists to a Liassic limestone from Bleiberg, in Carinthia, containing the remains of ammonites, which by their brilliant play of colour resemble precious opal. An argillaceous limestone, remarkably rich in dendritic markings, occurs in irregular masses in the Rhætic series, near Bristol, and has been polished under the name of *Landscape marble*. The *Ruin marble* of Tuscany is a soft argillaceous material, found near Pisa, and sometimes described as a kind of lithomarge. The *Ammonite* marble, found near Yeovil, is a brown Liassic limestone, rich in the remains of ammonites. The oolitic formation known as *Forest marble* takes its name from Wychwood Forest in Oxfordshire, which yields a coarse shelly limestone, occasionally polished as an ornamental stone. The famous *Purbeck* marble, extensively used in Gothic architecture, especially for slender clustered shafts, is a grey fresh-water limestone of Upper Oolitic age, crowded with *paludinæ*; whilst the *Sussex* marble is a similar shelly limestone, of fresh-water origin, occurring in bands in the Weald clay.

Stalagmitic marbles or *Onyx-marbles* (*q.v.*) consist of banded layers of calcite deposited from solution in caves. These were formerly called alabaster, and are now often known as 'Oriental alabaster,' the adjective being used to distinguish it from true alabaster, which is a native form of calcium sulphate (gypsum). Well-known varieties, often used for decorative purposes and small ornamental objects, are *Algerian onyx* and *Mexican onyx*.

Ophicalcite is a name applied to serpentinous limestones, which generally display clouded patterns, due to the interblending of a white limestone or dolomite with a green serpentinous mineral. The 'Irish green' of architects is a rock of this character from Connemara in western Galway. Of a similar nature are the serpentinous marbles of Anglesey, the eozoonal marble of Canada, and the verde antico previously mentioned. As the two constituents of an ophicalcite are unequally attacked by atmospheric agents, such a rock is unsuited for use in exposed situations, since it soon weathers to a rough surface.

In fact, marble generally is hardly suitable for outdoor work in large towns. The atmosphere of a city becomes charged with the products of the combustion of coal, including acid compounds of sulphur, and must sooner or later attack all marble monuments. It has been shown by Sir A. Geikie that marble slabs exposed in the churchyards of Edinburgh suffer total destruction in less than a century (Proc. Roy. Soc. Edinb. 1880, 10, 518).

A minor use of *marble* is *for the production* of carbon dioxide in soda-water manufacture. In the United States about 25,000 tons of scrap marble are annually ground into dust for this purpose.

References.—J. Watson, British and Foreign Marbles, Cambridge, 1916; J. A. Howe, Geology of Building Stones, London, 1910; G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903; S. M. Burnham, History and Uses of Limestones and Marbles, Boston, 1883; T. N. Dale, The Commercial Marbles of Vermont, Bull. U.S. Geol. Survey, 1912, No. 521; 1915, No. 589; A. Lee, Marble and Marble Workers, London, 1888; W. G. Renwick, Marble and Marble Working, London, 1909. L. J. S.

MARCASITE. An orthorhombic form of iron disulphide FeS_2, dimorphous with the cubic iron pyrites (*v.* PYRITES) and isomorphous with mispickel (FeAsS). Crystals are not infrequent, but their form is usually much obscured by twinning, producing more or less characteristic forms, which have given rise to the names 'spear-pyrites' and 'cockscomb-pyrites.' Stalactitic and nodular forms with an internal radiated structure are also common. The sp.gr., 4·8, is rather lower than that of iron pyrites, but the hardness (H.=6) is about the same. The colour is pale brass-yellow, rather lighter than that of iron pyrites (hence an old name 'white pyrites'), but the material frequently shows a surface tarnish. Marcasite is less stable than iron pyrites, and in a moist atmosphere it decomposes more readily, with the production of iron vitriol. When the material shows no crystal forms it is not always distinguishable from iron pyrites.

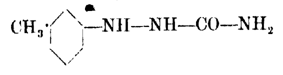
Marcasite occurs in mineral veins, as crystals and nodules in the chalk marl of Kent, in lignite and clay at Littmitz in Bohemia, &c. It is much less abundant than iron pyrites. When found in large amount it is used, like iron pyrites, for the manufacture of sulphuric acid and iron vitriol. L. J. S.

MARCASOL *v.* SYNTHETIC DRUGS.

MARC BRANDY OIL *v.* FUSEL OIL.

MARCTINE. Trade name for an antithermic $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$(1 : 3), *i.e.* methylacetanilide, in which the acetyl radical is replaced by the group $NH{\cdot}CO{\cdot}NH_2$. For reactions and tests, *v.* Lemaire, Rep. Pharm. 1907, 19, 49; J. Soc. Chem. Ind. 1907, 342.

MARETIN *m*-tolylsemicarbazide



Used as an antipyretic, *v.* SYNTHETIC DRUGS

MARGARIC ACID $C_{16}H_{33}COOH$ is stated to occur in the wax of lichens, and is obtained by boiling margaronitrile with alcoholic potassium hydroxide (Becker, Annalen, 102, 209; Heintz, J. 1857, 355).

MARGARINE (American, *Oleomargarine*) is the generic term for butter substitutes, consisting either of a mixture of animal fats alone, or of animal and vegetable oils and fats churned with milk to a butter-like emulsion, and coloured yellow (unless forbidden by law) with annatto, methyl orange, &c. During latter years, with the expansion of the margarine industry, two further kinds of 'margarine' have been brought into commerce, namely (1) margarine made exclusively of vegetable fats and oils churned to an emulsion with cow's milk, and (2) margarine made from vegetable oils and fats, wherein for cow's milk is substituted an emulsion made from kernels of almonds. Thus the last-named article consists exclusively of *vegetable* products and is sold under the name of 'nut butter' for the use of vegetarians. A variety of the last class of butter substitutes, no doubt suggested by the fact that their consistence was too soft, is made from a mixture of oleomargarine and milk of almonds (with an addition of sesamé oil, where prescribed by law).

The industry of butter substitutes owes its origin to experiments (induced by a prize offered by the French Government in 1869) made by Mège-Mouriès, which were worked out to a manufacturing process in Paris in the year 1870.

In the manufacture of the original margarine, as made by Mège-Mouriès's process, the animal fats used were oleomargarine—'oleo oil,'—and (or) neutral lard. Both ingredients must be prepared from the freshest beef fat and (or) hog-fat respectively.

For the production of oleomargarine, the rough fat is removed from the slaughtered animal as quickly as possible and brought into the works, where it is sorted. The kidney and bowel fats are selected, then carefully washed with warm water and thoroughly cleansed. The cleansed fat is brought immediately into large, well-aired, artificially cooled rooms to dry and harden (being allowed to hang there suspended from tin hooks for several hours), or is immersed in iced water in order to secure more rapid hardening. The hardened fat is then cut up and shredded in a shredding machine, and finally ground between rollers. The disintegrated mass is introduced into tin-lined jacketed vessels ('melting kettles') and brought to a temperature not exceeding 42°, this temperature being maintained by steam or hot water passing through the jacket.

At this temperature a portion only of the tallow contained in the tissue separates on the top of the comminuted rough fat. The settling and clearing is assisted by sprinkling salt over the surface of the melted fat. This melted portion, termed 'premier jus,' is run off into shallow tin lined trays arranged in tiers in a cooled room, when the bulk of the 'stearine' separates in a crystalline condition. The crystallised mass in the tins is cut up into square pieces of about 3 lbs. weight each, wrapped in canvas cloths, and placed in hydraulic or mechanical presses.

For the best qualities of margarine, the 'premier jus' is remelted at a temperature not exceeding 45° and allowed once more to settle out, after salt has been added, whereby the last remnants of membrane and tissue are precipitated. In large works the clear fat is allowed to run into wooden vats, in which it stands for from 3 to 5 days at a temperature suitable for the crystallisation of the 'stearine.' The whole is then stirred up into a homogeneous pulpy mass; this is wheeled in wooden waggons to the presses and treated as described already.

The oleomargarine, 'oleo oil,' which runs out from the presses formerly constituted the exclusive raw material for the manufacture of margarine.

In some works the rough fat from which the 'premier jus' has been taken off (in the manner described above) is heated once more to about 50°, when a second portion of fat is recovered. This is sold as 'secunda jus,' and is used in the manufacture of inferior kinds of margarine.

Amongst the vegetable oils, cotton-seed oil and cotton-seed stearine, sesamé oil, arachis oil, and recently even soya-bean oil, are preferred. According to the intended quality of the margarine, the quality of the cotton oil varies. In any case the cotton-seed oil must be practically devoid of free fatty acids, and rendered as free as possible from the peculiar flavour characteristic of this oil. The best brand of cotton-seed oil used for margarine making is known under the name 'butter oil.' Arachis oil (also olive oil) and sesamé oil are used to a greater extent in Europe than in the United States. Refined coco-nut oil and palm kernel oil are now incorporated to a very considerable extent with the fat stock of margarine.

A new source of solid fats has been made available for the manufacture of margarine by the development of the process of hydrogenating oil (*see* HARDENED OILS). The use of hydrogenated oils for this purpose was patented by Deveaux (Fr. Pat. 458611, 1913). In America cotton-seed oil hardened to the required extent is now frequently used in place of oleomargarine. Attempts have been made on the Continent to use hydrogenated fish oils in the manufacture of margarine, but the recurrence of the original odour renders these products unsuitable. In this country margarines containing hydrogenated oils are, as yet, only prepared for special purposes, such as for the use of bakers.

The oleomargarine, 'oleo oil' (and neutral lard) is mixed in *churning machines* at as low a temperature as is consistent with a semi-fluid condition with the vegetable oils and fats, and with milk.

The quality of the resulting product depends, to a great extent, on the quality of the milk and on its treatment previous to its admixture with the fats. The milk may be either sweet milk or sour. Sweet milk is more difficult to amalgamate with the oils and fats, and is retained with greater difficulty than soured milk, but the advantage the employment of sweet milk offers is that the resulting product has a finer taste and keeps better. The soured milk is, however, more easily incorporated with the fats and gives a higher yield. The proper treatment of the milk in the margarine works constitutes one of the most important features, just as the corresponding part of the butter-making process does in large dairies. The milk should be worked up as soon as possible after arrival. In any case it should be pasteurised immediately after it is received, and no preservatives—not even salt—should be used to prevent the fermentation of the milk. If the cream has not been taken off before the milk reaches the margarine works, it is removed (for butter-making) by means of a centrifugal machine, &c. The regular determination of the fat in the milk is necessary, not only for the proper control of the works, but also for the further reason that it has not infrequently occurred (on the Continent) that too much cream is taken off by the seller and replaced by sesamé oil, cotton-seed oil, or even by margarine.

The churning machines consist of oval, jacketed vessels provided with one or two sets of stirring and mixing gear. During the process of churning a constant temperature must be maintained by means of steam sent through the jacket of the churn. The object of churning, besides thoroughly mixing the ingredients, is to destroy the tendency of the oleomargarine to crystallise, and to pulverise ('atomise') the mixture, as it were, into single globules, such as butter-fat forms in milk. The art of the margarine maker at this stage of the process consists, therefore, in carefully regulating the inflow of milk and fat stock, so that a thorough emulsion is finally obtained.

First, the milk is put lukewarm into the churn and is mixed up with a little cream, followed by the addition of butter (if any be added). When the mass is thoroughly emulsified, part of the oleomargarine is added carefully, and when this has been properly incorporated with the emulsion, the oils required for the margarine stock are entered gradually and only then the remaining oleomargarine is mixed in. At this stage some manufacturers add colouring matters. The steam is then turned off, and the warm material cooled to a definite temperature by cold water being sent through the jacket.

In a process no longer used in up-to-date works, the cooled margarine leaving the churn was delivered into a tank and disintegrated by meeting a current of ice-cold water under pressure. This so-called 'wet' method has been practically superseded by the dry method.

The cooling of the still liquid margarine by running it off to a cooled table, has the serious drawback that the cooled mass is of uneven thickness, and hence an unevenly cooled product is obtained. This drawback is avoided by E. and H. H. Schou, who cool the margarine in a thin layer, of a thickness of about 1–1·5 mm., between two hollow cylinders which revolve in opposite directions and are cooled by a cold brine solution.

A large number of patents have been taken out for 'homogenising' or 'atomising' in special machines the mixture of milk and oils and fats. The merit claimed for these machines is that the product is more solid and has no 'oily' but rather 'a nut-like' taste. A drawback of all these apparatus is, however, that the margarine retains more water, and hence the proportion of fat falls below 80 p.c. Therefore in those countries where the maximum percentage of 16 p.c. of water is prescribed by law, the sale of such margarine would meet with difficulties.

In order to obviate this drawback, and at the same time to dispense with the kneading machines, in which the excess of the milk is removed, Schroeder (D. R. PP. 204061; 204062) carries out the blending and emulsifying process in three churning machines arranged one above the other and working in conjunction with an ‘atomiser.’ The temperature in the three churns through which the mixture of fats and milk passes is regulated carefully so that the completely emulsified contents of the lowest churn can be discharged on to a cooled table, where the mass solidifies to a thin layer, which is scraped off by a tangentially acting ‘doctor,’ so that the thin solidified film is curled up and discharged into a waggon. The ingredients forming the margarine are mixed (*v. infra*) in the proportion of 80 parts of fats and oils, 16 parts of milk, and 4 parts of cream, consisting approximately of one-third of butter-fat.

Among other more recent types of emulsifiers mention may be made of that of Silkeborg (Eng. Pat. 4657 of 1914) and that of Blichfeldt (Eng. Pat. 18048 of 1914). The former consists of a horizontal cylinder surrounded by a heating jacket, and containing a rotating agitator, which drives the mixture of milk and fat against fixed baffle plates containing perforations, which effect fine subdivision of the mass.

In Blichfeldt's apparatus the emulsification is effected by means of a rotating disc pierced with slots, which is mounted on a hollow shaft in a vessel the walls of which are close to the disc. The milk is introduced through the hollow shaft, whilst the melted fat is delivered through an opening in a tube passing across the vessel. The use of these newer types of emulsifiers permits of the process being carried out continuously, and thus effecting an economy in space, power, and time.

In the now practically obsolete ‘wet’ method of cooling the emulsion water chilled to a low temperature by refrigerators is used as the cooling medium. Various modifications of cooling devices are also in use. For example, in Rasmussen's apparatus (Eng. Pat. 29831 of 1913) the fatty mixture is distributed on to a hollow cylinder which rotates in cold water, at a depth of about two-thirds its diameter. The congealed fat is then removed from the surface by means of scrapers which deposit it on a travelling band.

In the ‘dry’ method of chilling the emulsion the mixture may be distributed on to a travelling band which traverses a current of cold filtered air (Eng. Pat. 20292 of 1911), this method, however, being too expensive for use; or, as in Christensen and Lauridsen's process (Eng. Pat. 20568 of 1912), it is distributed as a thin film on the surface of a rotating cylinder, through the interior of which chilled brine circulates. In Schou's cooling drum (Eng. Pats. 12561, 1907, and 1160, 1909) brine chilled to -7° is circulated through cylinders revolving in opposite directions, and capable of being adjusted so that a desired thickness of film can be obtained. A similar type of apparatus has been patented by Jurgens (Eng. Pat. 10868 of 1914). After being chilled in this way margarine frequently has a crystalline structure, and requires a final mechanical kneading to give it the consistence of butter.

Effective emulsification depends upon the correct application of the principles of colloidal chemistry. For an outline and discussion of these principles reference may be made to W. Clayton's ‘Margarine’ (Longmans, 1920).

The solidified margarine is now kneaded to a butter-like mass by means of rollers contained in cylindrical rotating drums. The margarine is thus thoroughly worked through, and the excess of water squeezed out, so that a homogeneous mass results. This is then salted to taste, mixed with a little colouring matter (if permitted by law), and again submitted to thorough kneading in a second set of kneading machines of the same or of different type, in order to produce the required texture throughout the whole mass. The mixture with salt, preservatives, &c., is usually effected by means of a blending machine. The margarine is finally moulded into lumps, pats, rolls, or any other desired shape.

As an example of a good working recipe for margarine the formula officially proposed in 1918 may be quoted, viz., Premier Jus, 15; coconut oil, 15; palm-kernel oil, 50, arachis oil, 10; and cottonseed oil, 10 p.c. This melted at about 25°. For winter use the formula was modified so as to contain 30 p.c. of liquid oils, 20 p.c. of animal fats, and 50 p.c. of vegetable fats.

The object of the margarine maker being to render his product as closely similar to butter as possible, and to take away the ‘tallowy’ or too strongly ‘oily’ taste of the material, some manufacturers (provided the law permits) add cow's butter. Others add small quantities of volatile acids, volatile aldehydes, mixed glycerides containing butyric acid, such as dibutyromonostearin and dicaprylomonostearin, or ‘butter perfumes,’ which consist chiefly of volatile acids, such as propionic, butyric, caproic, and their ethyl esters. Also coumarin (sold as an emulsion with sesame oil) would fall under the head of ‘perfumes.’

It should, however, be stated that margarines prepared from the best material and in an unobjectionable manner do not require any of these additions. The latter are chiefly used in order to mask low grade materials, or to afford analytical data which may create a fictitious impression as to the real nature of the product.

An important point in the manufacture is to produce margarine which will froth and ‘brown’ on heating, so that even in cooking the margarine may resemble butter. Since the property of butter to brown and froth is due to casein and milk sugar, it is evident that the more milk is used in the manufacture of margarine, the nearer will the product approximate to butter.

Milk is liberally used in this country and in America; but in some continental countries where the law forbids the addition of more than a strictly limited quantity of milk, a number of patents have been taken out for substances which are credited with imparting to margarine the desired properties. Prominent amongst these patented products are casein and other proteins. Some patentees claim cholesterol and cholesteryl esters, or lecithin. Lecithin is now incorporated with margarine in the form of egg yolk, which is, of course, cheaper than lecithin.

Vegetable waxes have also been proposed as admixtures, and the use of beeswax for this purpose has even been patented, although the addition of such substances must seriously interfere with the digestibility of the margarine.

Besides the taste, the consistence also plays an important part in the valuation of margarine. If the finished margarine has not been worked sufficiently on the tables, its consistence may be either too 'greasy' or too 'sandy,' *i.e.* the semi-crystalline mass has not been properly 'broken,' and its grain differs from that of a properly prepared dairy butter. Some margarines are also finally mixed with a little glycerin, or glucose, or sugar, in order to improve the texture or to give them a glossy appearance and also a sweeter taste. The addition of glucose or cane-sugar must, however, be considered a mistake, as this only leads to premature development of fungus on the margarine.

The manufacture of butter substitutes is differently affected by legislation in different countries. In this country the adding of butter to margarine in any proportion was at first allowed; for, according to the Margarine Act of 1887, any 'butter' containing even the smallest quantity of foreign fat was looked upon as margarine. By the Margarine Clause of the Food and Drugs Act, 1899, however, the maximum proportion of butter-fat in margarine has been restricted to 10 p.c.

This restriction has been confirmed by the Butter and Margarine Act of 1907, and it has been further enacted that margarine must not contain more than 16 p.c. of water. Margarine factories must be registered, and be open to Government inspection. Prohibited preservatives must not be used, nor is an excess of boric acid allowed. According to the same Act 'margarine' means 'any article of food, whether mixed with butter or not, which resembles butter, and is not milk-blended butter.' For the latest enactments in other countries the reader is referred to Lewkowitsch, Chemical Technology.

In the *examination* of margarine the determination of the Reichert-Meissl value constituted the most important characteristic, as it indicated in the briefest and surest manner the amount of butter-fat contained in the margarine, either added as butter or originating from the milk which had been incorporated with the oils and fats in the process of manufacture. Since, however, considerable quantities of coconut oil and palm-kernel oil form ingredients of margarines, and since even margarines are made at present which consist exclusively of the last-named two fats, without even an addition of cow's milk, the indications of the Reichert-Meissl value no longer have that importance which they formerly possessed.

The Polenske value, which is based on the determination of the volatile insoluble fatty acids which distil in the determination of the Reichert-Meissl value, affords a more trustworthy indication (Analyst, 1904, 29, 154; 1911, 36, 333, 336). The method of Shrewsbury and Knapp (Analyst, 1910, 35, 385) is based upon the fact that the predominating fatty acid (lauric acid) of coconut oil is readily soluble in dilute alcohol, and may be estimated by titrating the solution with standard alkali solution. Kirschner's extension of the Reichert-Meissl-Polenske method (Zeitsch. Nahr. Genussm. 1905, 9, 65) is essentially an estimation of the amount of butyric acid present. It has been shown by Revis and Bolton (Analyst, 1911, 36, 336) that by determining this value it is possible to ascertain rapidly whether butter-fat is a constituent of a margarine. The relationship between the Kirschner, Reichert-Meissl and Polenske values has been worked out by Bolton, Richmond and Revis (Analyst, 1912, 37, 183), and more fully by Cranfield (Analyst, 1915, 40, 339). According to Richmond (Analyst, 1919, 44, 166), results agreeing with the mean figures are obtained by the use of the equation $P = 0{\cdot}26(K - 14)$, where P and K represent the Polenske and Kirschner values respectively. At one time margarine was adulterated with paraffin wax. The separation and identification of unsaponifiable matter in the fat would detect this fraud.

A test to distinguish between butter and margarine is to examine a thin layer of the fat under the microscope, using polarised light, when margarine showed a crystalline appearance (C. Williams). This test, however, fails in the case of 'renovated' or 'process' butters (W. Clayton, J. Soc. Chem. Ind. 1917, 36, 1205).

On heating the clear filtered fat from butter or margarine to a temperature of about 185° the natural butter colour and vegetable colours are destroyed, whereas coal-tar colours are not.

For an account of the occurrence of vitamins in butter and margarine and their significance from a nutritional point of view, *see* Clayton's 'Margarine.' J. L.

MARICOL. Trade name for magnesium ricinoleate.

MARINE ACID. *Syn.* for hydrochloric acid (*q.v.*).

MARINE ANIMAL OILS *v.* OILS.

MARIPA FAT. The fat of the fruit of *Maximiliana* [*Attalea*] *Maripa* (Drude), used in the West Indies as butter. It is employed in French Guiana as a medicinal liniment, and is practically identical with coco-nut fat in characters.

MARJORAM, *Origanum Majorana* (Linn.), a herb employed in flavouring. It is generally used in the air-dried state, when it has the following composition:—

Water	Protein	Fat	Ethereal oil	N-free extract	Crude fibre	Ash	Sand
7·6	14·3	5·6	1·7	35·6	22·1	9·7	3·4

Commercial dried marjoram often contains much sand; a good sample should not contain more than 14 p.c. of ash, of which not more than 3·5 or 4·0 p.c. should be insoluble in hydrochloric acid. The following analyses of the ash of marjoram were made by Rupp (Zeitsch. angew. Chem. 1892, 681):—

	K_2O	Na_2O	MgO	CaO	Fe_2O_3	Mn_3O_4	P_2O_5	SO_3	Cl	CO_2	Sand
German	20·2	0·7	4·8	17·6	7·3	1·0	8·9	4·9	2·1	6·1	26·5
French .	18·3	0·7	6·7	24·8	6·1	trace	9·1	4·8	1·5	8·6	19·4

(*v.* OILS, ESSENTIAL). H. I.

MARKASOL. *Bismuth borophenate* (*v.* BISMUTH, ORGANIC COMPOUNDS OF).

MARKING-INK is used for stamping or marking fabrics, and should be permanent, and indestructible to the material. The basis of many marking-inks is a silver salt dissolved in aqueous ammonia containing a little gum. This is only coloured on decomposition, so a little dye is needful; dark-brown inks contain archil and chlorophyll, crimson contain carmine, whilst copper sulphate is an ingredient of blue ink.

Redmond's ink is made thus: dissolve 3 oz. 2 drms. silver nitrate and 3 oz. sodium carbonate each in 2 pints boiling water, mix, and collect the precipitate so formed on a filter, wash with water, transfer to a mortar, add 10½ drms. tartaric acid, triturate the whole, and when effervescence has ceased, add 3½ oz. of ammonia (0·880), stir until dissolved, and add 1½ oz. powdered white sugar. Mix 1 oz. chlorophyll and 1 oz. archil with 4 oz. water, add 2½ oz. of acacia gum to this when dissolved, strain, add to the ammoniacal solution and make up to 20 oz. with water. This ink, if carefully prepared, contains only the tartrate of silver; on heating metallic silver is left on the fabric.

An indelible ink is made by dissolving 1 oz. silver nitrate and 1½ oz. of sodium carbonate separately in 3 oz. distilled water; mix the solution, collect and wash the precipitate with distilled water. Add 160 grs. tartaric acid, dissolved in 1 oz. water, to the precipitate in a mortar, stir until effervescence ceases, and then add 2 oz. liquid ammonia to dissolve the precipitate. Mix in 80 grs. aniline black, dissolved in 1 oz. boiling water, and add 5 drms. glycerol and water to make up to 8 fl. oz. (Spon's Workshop Receipts, 1909, 510).

Aniline marking-ink is prepared thus: in two bottles (1) add 1 fl. drm. aniline and 10 grs. toluidine to 2 fl. drms mucilage of acacia and dilute hydrochloric acid, and mix; (2) powder 40 grs. cupric sulphate, 20 grs. ammonium chloride, 20 grs. potassium chlorate, and dissolve in 6 fl. drms. water; lastly, add 2 fl. drms. of thick mucilage and mix. Leave for 2 or 3 days before using. Equal parts of each solution are mixed immediately before using and applied with a quill pen (Scient Amer. Ency. 1903, 276). Single solution aniline inks are also made.

An ink suitable for rubber stamps, as it dries rapidly, is made by adding 15 oz. glycerol to a solution of ½ oz. aniline black and 15 oz. pure alcohol.

To use silver marking-ink for stamping, add to 1 oz. ink, 1 drm. glycerol and 1 drm. treacle.

To make an indelible red ink, dissolve 2 oz. shavings of dry white curd soap in 1 part balsam of copaiba by heating, add sufficient vermilion and stir occasionally until cold.

Indian-inks are used for marking.

An ink suitable for labels which cannot be bleached is made by mixing equal parts of pyrogallol and iron sulphate. The label is varnished when dry (Hiscox, Receipts, 1907, 407).

The juice of the banana and of the marking-nut have to some extent the properties of marking-ink, but no practical method of preparing them for sale has been developed.

MARL (Ger. *Mergel*), a name properly restricted to calcareous clays, but frequently extended so as to include any clay which, when dry, is readily friable. Thus the Keuper or New Red Marls, of Triassic age, often contain little or no calcium carbonate. An analysis of a red Keuper marl, from Worcester, by Voelcker, yielded 4·85 p.c. of lime. The typical marls are soft, earthy, and of a white, grey, or brownish colour. Many of them disintegrate in water; and they are readily attacked by dilute hydrochloric acid with evolution of carbon dioxide. Marls have been used for ages by agriculturists for the purpose of improving certain lands, the material for 'marling' being systematically dug from 'marl pits.' Since a marl is a calcareous clay, it may obviously pass into an argillaceous limestone; the *chalk-marl* is a rock of this kind. When a marl becomes indurated it is often known as *marlstone* or *marl-rock*, and the hard beds of the Middle Lias, which in Yorkshire yield the Cleveland iron ore, are recognised by geologists as the 'marlstone.' A laminated variety of hardened marl is termed *marl-slate*, which readily passes into a calcareous shale. The marl-slate occurring in the Permian series in the north of England is equivalent to the German *Kupferschiefer*, a bituminous marly shale, containing copper ore. The *shell-marl* found at the bottom of certain lakes, especially in Scotland, is a calcareous ooze, consisting largely of organic remains. L. J. S.

MARMATITE *v.* Zinc-blende.

MARRUBIIN *v.* Marrubium.

MARRUBIUM, *Horehound, Hoarhound.* (*Marrube blanc*, Fr.; *Andornkraut*, Ger.) Horehound has been employed for its mild tonic, stimulant, and laxative properties, especially in domestic medicine, for a long period. It consists of the leaves and tops of the *Marrubium vulgare* (Linn.), a perennial herb growing throughout most parts of Europe, Asia, and America (Bentl. a. Trim. 210). The only constituent which has been examined, except a trace of *volatile oil*, is the bitter neutral *marrubiin*.

Marrubiin was examined by Gordin (J. Amer. Chem. Soc. 1908, 30, 265, where *see* earlier literature), who assigned the formula $C_{21}H_{28}O_4$, m.p. 155°; b.p 297°-299°/15 mm.; $[a]_D+45{\cdot}68°$, forms large crystals from alcohol. It is the lactone of *marrubic acid* $OH{\cdot}C_{20}H_{28}O_2{\cdot}CO_2H$, m p. 173°–174°, which can be reconverted into marrubiin in several ways. G. B.

MARSH GAS. *Methane* or *methyl hydride* (*v.* Methyl).

MARSH-MALLOW GUM *v.* Gums.

MARSH-MALLOW ROOT contains 1·7 p.c. of an oil composed of palmitin and olein, butyric acid, a phytosterol, apparently identical with sitosterol, a hydroxy acid of high molecular weight, an odourous substance of unknown composition, a lecithin containing palmitic and oleic acids and choline, 10·2 p.c. of sucrose and 0·78 p.c. of invert sugar, a mucilage ($(C_6H_{10}O_5)$), consisting of glucosan (64 p.c.) and xylan, and another saccharocolloid giving *d*-galactose on hydrolysis (von Friedrichs, Arch. Pharm. 1919, 257, 288).

MARSH ROSEMARY. *Andromeda Polifolia* (Linn.); also an American name for *Statice caroliniana* (Walt.) [*S. Limonium* (Linn.)]. *Andromeda Polifolia*, belonging to the *Ericaceæ*, is the only British species of the genus; it is found also in peat-bogs throughout the north of Europe, Asia, and America. It is an acrid narcotic and is fatal to sheep pasturing off it.

Statice caroliniana is found in marshy situations from Maine to Florida. According to Parrish, it contains 12 p.c. of tannin and has been used in the manufacture of leather.

MARTENSITE. The principal constituent of all hardened steels containing over 0·16 p.c. of carbon. It is a solid solution of carbon in iron; when saturated, as in high-carbon steels, it is known as '*hardenite*' (Howe).

On a polished surface, etched with picric acid, it shows under the microscope three systems of cleavage planes inclined to each other at 60°. It is very hard and cannot be scratched by a needle

Martensite is magnetic and forms one of the principal constituents of permanent magnets

MARTIUS'S YELLOW. A synonym for Naphthalene yellow; known also as *Jaune d'or, naphthol yellow, Manchester yellow.* The sodium or lime salt of dinitro-α-naphthol (*v.* NAPHTHALENE).

MASOPIN RESIN *v.* RESINS.

MASS ACTION *v.* CHEMICAL AFFINITY.

MASSECUITE *v.* SUGAR.

MASSICOT *v.* LEAD.

MASSICOTITE *v.* LITHARGITE.

MASTIC CEMENT *v.* CEMENTS

MASTIC RESIN *v.* RESINS.

MASTIC VARNISH *v.* VARNISH.

MATAZIETTE. A name given to an explosive made in Switzerland, formed of nitroglycerin, sand, and chalk, coloured with ochre.

MATCHES. (Ger. *Zundholzer, Zundholzchen*; Fr. *Allumette*; Sw. *Tandsticka*, pl. *Tandstickor*; Du. *Zwavelstokje, Fosforus-stokje*; It. *Zolfanello, Fiammifero*; Da. *Svovlstik*; Hung. *Gyufa.*)

Derivation and variants of the word 'match.'—Older Eng. forms, *me(c)he, metch, matche. mache, macche*; O. Fr. *mesche, meiche*; Mod. Fr. *mèche*; Pr. *mecca, mecha*; Catal. *metxa*; Sp. and Port. *mecha*; It. *miccia*; perhaps from Gr. μύξα, L. *myxa, mixa, myxus*, lamp-nozzle, lamp-wick, mucus of the nose; connected with L. *muccus*, nasal mucus, whence It *moccolo*, L. *mucculus*, snuff of a candle.

Definitions. 1. (*Ordinary language*).—An instantaneous fire-producer, consisting of a short stem, rod, or tube, tipped at one or both ends with a composition or paste, inflammable by friction; or (as in the earlier forms) when brought into contact with a chemical reagent.

2. (*Military and mining*).—A cord or thread impregnated with combustible material, capable of burning along its entire length, so that fire can be conveyed from one point to another. This kind of match, which is better termed a fuse, is not ignitable by friction, and may be 'slow' or 'quick,' according to requirements.

I. FRICTION MATCHES.

History and development. Friction matches are among the most useful products of the period immediately preceding the Victorian age, and afford a signal instance of the ministration of science to human needs. Developed in less than three-quarters of a century from fire-producing appliances of the most primitive types, they have been so perfected that it is difficult to foresee in what direction further progress is possible.

Since the discovery of phosphorus in 1673 by Brand, of Hamburg, many attempts had been made to obtain light and heat expeditiously by its aid; one of the earliest consisting in rubbing a particle of phosphorus between folds of coarse brown paper, the flame produced igniting a sulphur-tipped splinter of wood. This plan was found to be inconvenient and dangerous, and phosphorus gradually fell into disuse. After the element had been, in a technological sense, left severely alone for more than a century, renewed attempts were made to utilise it. One contrivance was the somewhat impracticable '*phosphoric taper*' (1781). This was of wax, enclosed in a sealed glass tube, at one end of which was a fragment of phosphorus. After the tube had been dipped in warm water, the end remote from the phosphorus was cut off with a file, the taper was withdrawn, with some phosphorus adhering to it, which spontaneously inflamed. Another appliance was the '*phosphorus bottle*' of Cagniard de Latour (1810), containing partially oxidised phosphorus, some of which was withdrawn by a brimstone match, dipped into the phial, and then ignited by friction. A '*briquet phosphorique*,' brought out in Paris in 1786, consisted of a small tin box containing sulphur-tipped matches, together with a bottle coated internally with phosphorus. '*Pocket luminaries*,' soon afterwards sold in London, and '*portable fire boxes*' were similar. Various early devices for quickly producing fire were Homberg's '*pyrophorus*' (an oxidisable powder, free from phosphorus, prepared by roasting alum with flour, honey, or sugar, and inflamed by exposure to air), and Döbereiner's pyrophorus, of similar character; '*pneumatic tinder-boxes*,' containing amadou or ordinary tinder, ignited by the heat generated when air was compressed by a piston, such as Mollet's Pump, and Lorentz's '*light syringe*' (1807); '*electropneumatic fire-producers*' (invented by Brander, 1778, and by Fürstenberger, 1780), in which hydrogen was kindled by an electric spark - to which category belonged Mayer's apparatus - (1811); Volta's '*inflammable air lamp*'; Fyfe's '*hydropneumatic lamp*'; and, lastly, Döbereiner's '*platinum lamp*' (in which contact with spongy platinum, or iridium, ignited hydrogen gas)—with Eisenlohr's, v. Babo's, v. Römer's, Palkl's, Hare's, Schiele's, and Böttger's modifications of the same.

The principal stages in the evolution of matches will now be referred to in chronological sequence. During the year 1804, phials charged with a mixture of phosphorus, wax, and oil were sold in cases containing also some brimstone-tipped matches and a piece of cork. The matches were dipped into the mixture, withdrawn, and ignited by friction on the cork. In 1805, Chancel, of Paris, applying the principle discovered by Berthollet, of oxidation by chlorates in the presence of strong acid, invented '*oxymuriate matches*,' strips of wood tipped with a mixture of potassium chlorate, sugar, and gum, ignited by contact with sulphuric acid. In the same year, according to Niklés, *friction matches* containing the element phosphorus were made and used in Paris. In 1806 various improvements in the tinder-box were suggested by Phillips, who was followed by Lorentz (1807), with an apparatus for igniting hydrogen gas by the aid of an electrophorus, and with the 'light syringe' already mentioned (same patent). In

1809, to Derepas, of Paris, was granted a French patent 'for a peculiar composition of phosphorus match lights.' This was an attempt to render phosphorus more manageable and less inflammable, by intimately mixing 8 parts, 'half melted,' with 4 parts of magnesia. When cold, the substance was described as forming 'an opaque body fit for inflaming a common match' (Description des Brevets). During the year 1812, '*chemical matches,*' manufactured according to Chancel's invention, began to be sold extensively, a hundred for a florin, in Vienna. The sticks were tipped with potassium chlorate, sugar, and gum, or with the same ingredients and lycopodium; *colophony, gum benzoin*, &c., were also used. *These matches, packed in suitable cases, together with bottles* containing asbestos soaked in sulphuric acid (in accordance with a proposal made in 1812 by v. Romer, of Vienna), were sold more widely on the Continent than any others, up to the year 1844. Among the makers were v. Romer, Peters, Wagner, Siegel, Ehrlich, and Merckel. The cases were known as '*tunkfeuerzeugen,*' '*briquets phosphoriques,*' '*inflammable match-boxes,*' '*instantaneous light boxes,*' '*phosphorus boxes,*' &c.; and one form was prominently sold in this country as Heurtner's '*Eupyrion.*' Violence of combustion, and liability of the acid to be spurted about, were characteristics of these matches. In 1816, friction matches tipped with a composition containing phosphorus are stated to have been manufactured in Paris by François Dérosne, who by Gintl and others is regarded as the first maker of the phosphorus friction-match. The year 1823 is marked by the invention of the Döbereiner lamp, already referred to. About this time, too, were used, at Erfurt, in Prussia, small glass tubes containing equal quantities of phosphorus and sulphur carefully fused together, into which thin sticks or splints of wood were introduced, easily inflamed afterwards by friction. The early attempts to make friction matches in Paris and elsewhere appear to have failed completely; and the honour of having invented, in 1827 or earlier, the first practical and useful matches ignitable by friction, indisputably rests with an Englishman, John Walker, of Stockton-on-Tees, Durham (*d.* 1859). Walker was an apothecary, who had been apprenticed to a local surgeon before starting in business as a druggist. He was much interested in experimental chemistry, and for some years prior to 1827 had been preparing and selling, under the name of 'percussion powder,' dried mixtures of potassium chlorate and antimony sulphide, made up with gum-water. Eventually it occurred to him to dip splinters of wood into such a composition, and to supply these matches in tin boxes, together with a piece of folded glass-paper, under the name of 'friction-lights.' Samuel Jones, of 201, Strand, London, who from 1829–1830 onwards sold imitations of Walker's matches under the designation of '*lucifers*' (a name always repudiated by Walker), publicly announced in 1831 that about a year previously they had been 'lectured on at the London and Royal Institutions.' Matches resembling Walker's, but mostly sulphur-dipped, were made also by Jones's competitor, G. F. Watts, in 1831 ('*Watts's chlorate* or *lucifer matches*'), and by Richard Bell & Company in 1832 ('*improved lucifers*'). Watts and Bell both 'borrowed' the name 'lucifer' from Jones. '*Allumettes infernales*' were brimstone-dipped matches of the same type; and German matches of a similar kind, but not sulphured, were also manufactured. H. Link's '*allumettes chémiques,*' produced in Germany for the French market, and L. Acaleitner's (Salzburg) '*snellzünder,*' were of like character. Among French makers of matches of an allied type were J. Joseph et Cie (1833), and A. Perpigna (1834).

Though non-phosphoric, Walker's matches inflamed when pressed between the folds of the glass paper and sharply withdrawn. Thus ignitable by friction, they were the lineal ancestors of twentieth-century matches.

Walker at first used strips of cardboard for the stems of his matches, but later he substituted splinters of wood, which he employed the poor people of the district to cut.

In the year 1828, Samuel Jones patented the '*prometheans,*' a return to the principle of the oxymuriate match. These consisted of slightly tapering, spirally-rolled paper tubes, containing in the broader or ignition end a minute fusiform glass tube (not a bulb, as usually stated), 10·5 mm. long by 1·0 mm. wide which enclosed a dark-blue liquid, shown by the writer's analysis to be composed of sulphuric acid coloured by indigo. The glass vessel was imbedded in a composition, variously stated to contain potassium chlorate and sugar, 'fulminate,' &c., but found by the writer to be composed of potassium chlorate, lycopodium, and sulphur. Neither sugar nor fulminate was present in the prometheans examined.

'*Lucifer matches*' or '*lucifers,*' *i.e.* non-phosphoric matches, of Walker's type, which inflamed when rapidly drawn through folded sand- or glass-paper, were followed in the early thirties by non-phosphoric friction matches, which could be ignited, though with difficulty, by being *struck upon rubbers affixed to the boxes.* Such were the friction matches made by Savaresse and Merckel (Paris), the igniting composition of which was a mixture of potassium chlorate, antimony sulphide, sulphur, and gum. The rubbing surface was composed of potassium chlorate, minium, pumice, and gum. Similar non-phosphoric friction matches were patented in 1832 by Siegel, an Austrian manufacturer; and Link's 'Chemische Streichfeuerzeuge' were of a like description. Matches, capable of being struck upon the box, soon became known as '*Congreves,*' both in this country and abroad; and the name was applied to the phosphoric friction matches which next came on to the market. 'Congreves' succeeded to 'lucifers'; 'lucifers' followed 'friction-lights'; 'friction lights' superseded 'chemical matches.'

It may be mentioned here that Samuel Jones seems to have been the first user of the word *fuzee*, or fusee, as applied to a match for lighting pipes or cigars. But Newton, a few months earlier, applied the term to a match for use by 'smelters.'

Hare's pyrophorus, described in 1831, was made by heating Prussian blue to redness in a glass tube, which immediately afterwards was hermetically sealed. On breaking the tube and throwing out the contents they took fire.

Efforts meanwhile were being made to produce a practicable and satisfactory friction match, in which *phosphorus* should take the place of antimony sulphide; and this important result appears to have been achieved simultaneously in several different places during the period 1831–1833. At all events, in 1833–1834, v. Römer, Preschel, and Siegel, in Vienna, and Moldenhauer, at Darmstadt, were manufacturing wooden friction matches, the igniting compositions of which contained phosphorus. The date of v. Romer's patent was January 4, 1834. Other pioneer makers, associates or otherwise of the above, were Pollak and Kreutz (Vienna); Anthon (Darmstadt); and Amüller (Waiblingen). Many of these early continental makers called their matches 'congreves.' In France, the invention of the phosphorus friction match is now generally attributed to Dr. Charles Sauria, of St. Lothair (*d.* 1895), who, in January, 1831, while a student at the College d'Arc, Dole (Jura), made very good friction matches containing phosphorus, but neglected to protect his invention. Sauria's claims have been well attested; and it is possible that a rumour of his experiments somehow was conveyed to other countries during the few months following the discovery. The French Government in 1884 recognised 'L'Invention des Allumettes Chimiques' by a grant to Sauria of a '*bureau de tabac*,' the Academie Nationale Agricole bestowed upon him a medal, and during the year 1896 there was a movement to set up a monument to him in Paris. The design was not carried into execution, however. J. F. Kammerer (*d.* 1857), of Ludwigsburg, Wurtemburg, is in Germany usually credited with having invented phosphorus friction matches in 1833, and he is said to have worked out the idea during the previous year; but the invention was not protected, and was pirated in every direction. Claims have been advanced also for a young Hungarian student at the Vienna Polytechnic School, named János Irinyi (who in 1895 was still living in south Hungary). He is alleged to have made the discovery in 1835, and to have sold his process to v. Römer. Possibly Irinyi's invention marked an advance upon the type of phosphoric friction match which had already begun to be manufactured. Lastly, a professor at the Technical High School in Stockholm, Dr. J. S. Bagge, between 1830–1840, worked out a method for procuring light by means of phosphorus friction matches, and drafted directions for their manufacture.

The oxidising agent used in the earliest matches was potassium chlorate only, but in 1835 Trévany partly replaced it, as being too violent in its action, by a mixture of minium and manganese dioxide.

In the United States of America the first patent for the invention of phosphorus friction matches was granted in 1836 to A. D. Phillips, whose igniting composition was a mixture of phosphorus, sulphur, chalk, and glue. In 1837, v. Romer substituted lead peroxide for potassium chlorate; in 1838, Preschel and Kreutz patented a composition consisting of phosphorus, manganese dioxide, nitre, and gum arabic; Beyer (Vienna, 1838) and Riess (Vienna, 1843) used as the oxidising agent a mixture of minium and nitric acid; and in 1842–3, Böttger, of Frankfort, recommended the substitution, for potassium chlorate, of mixtures of minium and saltpetre, or of lead peroxide and lead nitrate. Moldenhauer, about the year 1838, introduced the use of calcined magnesia in order to counteract the effects of the formation of hygroscopic oxidation-products of the phosphorus; and chalk also (introduced in 1836 by Ehrlich, of Prague) was used for the purpose. Preschel and Klug (1837) endeavoured to accomplish the same end by coating the match-heads with resinous spirit-varnishes. Between 1820 and 1840 various machines for cutting the wooden stems or 'splints' rapidly and in large quantities, were introduced; and the match industry has since developed in country after country until it is now of very great magnitude and world-wide importance. Although in the conditions and processes of manufacture, as well as in the character of the materials used (especially during the past 25 years), there have been improvements and modifications, so far-reaching and gigantic that the industry may be said to have been revolutionised, nevertheless the ordinary friction match of to-day is not *essentially* different from the 'lucifers' and 'congreves' made during the first third of the 19th century. But the use of machinery has been greatly extended. Continuous and automatic machines are at the present time widely and increasingly employed; and, following upon a gradual diminution in the proportion added, in only a very few countries now is white or yellow phosphorus used at all in the manufacture (*see post*, pp. 230 and 235). In 1855 J. R. Wagner recommended that less phosphorus should be used, and experimented with barium nitrate and potassium dichromate, as oxidising agents. The latter salt he considered too costly, and he remarked that lead dioxide, though more expensive and no better, had then largely replaced the mixture of minium and manganese dioxide. In view of the subsequent introduction and present widespread use of tetraphosphorus trisulphide, or phosphorus 'sesquisulphide,' P_4S_3, it is interesting to record that in 1860, Puscher, of Nuremberg, introduced the use of phosphorus sulphide instead of phosphorus, but found few followers. Bals (D. R. P. 89700, 1896) also tried a fused mixture of sulphur and red phosphorus. For making matches *waterproof*, Zimmermann (1864) used collodion, as an improvement on the resinous varnishes of Preschel, Klug, Winterfeld (1842), and Krutzler. Barker (1845), and, after him, Gaillard, applied a coating of sulphur over the friction composition, such matches being found by Abel (1863) to be waterproof, but somewhat difficult to ignite. Hannan and Mills (1882), for the same purpose, mixed paraffin, fatty bodies, or resins, with the compositions. The inventions of Thomas (1895), Fowler and Bower (1895), and Ramsden and Hirst (1900), had a similar end in view. *Scenting ingredients*, such as gum benzoin, frankincense, &c., were often added to the varnishes; and in 1854 Krakowitzer, of Pottenstein, Austria, introduced a process by which a metallic lustre was imparted to the heads of matches '*de luxe*,' or 'parlour' matches (containing lead compounds), by exposing them to sulphuretted hydrogen gas. This process was modified by J. Ginzky in 1860, and again by Schindler, in 1867. A later improvement (A. Kielmeyer, 1879) was to varnish over the silvered heads with an alcoholic solution of colophony, shellac, &c., to which an aniline or other dye was added. Thus, to obtain a greenish bronze, Kielmeyer used fuchsine or methyl violet; other colours employed were methyl green, aniline orange and the like.

Great as was the improvement effected by the substitution of phosphorus for the less easily oxidisable antimony sulphide, there were serious disadvantages attending its use. The poisonous nature of phosphorus, the somewhat too ready inflammability of the igniting compositions made with it, and especially the 'phosphorus disease' (a carious affection of the lower jawbone, leading to necrosis, from which a small proportion of the workers—especially the dippers—were liable to suffer), were much the most important of these. The phosphorus disease, first described in 1845 by Lorinser, of Vienna, has intermittently called for the anxious attention of manufacturers and statesmen in most countries where white phosphorus has continued to be used in match-making, from 1870 to the present time. Shortly after it had been found that satisfactory friction matches could be produced without the use of yellow phosphorus, legislation was introduced in all the principal countries of Europe and America whereby the use of yellow phosphorus in this industry was prohibited, with the result that phosphorus necrosis may be said to be a thing of the past so far as the manufacture of matches is concerned. Good ventilation, impregnation of the air of the factories with the vapour of oil of turpentine, and scrupulous personal cleanliness on the part of the operatives, combined with particular attention to the condition of their teeth, were found greatly to diminish the number of cases of necrosis. It was shown by Thorpe and Tutton that the disease was caused by the direct action of the vapour of phosphorus oxide P_4O_6 on the bone, and that the characteristic smell, noticeable in the dipping-room of a match-factory where white phosphorus was used was due, not to the vapour of the element phosphorus, but to the fumes of phosphorus oxide. Only those workers with carious teeth are liable to suffer from necrosis of the jaw. Recognising the bad state of the teeth of many of their workers, Messrs. Bryant and May, in London, and the Diamond Match Company, Liverpool, years before white phosphorus had ceased to be used, were the first match manufacturers to take the important preventive step of establishing dental departments, where all the workers could be treated free of charge. This great benefit to the workers is still available at the factories, although the use of white phosphorus in Great Britain has for a long period been discontinued. In the annual report of the German inspectors of factories for 1879 it was stated that, in that year, among 5724 workmen coming in contact with phosphorus vapours, only nine cases of necrosis were observed, six of illness, and three of death (Jettel, Chem. Zeit. 1883, 7, 89). In 1884, however, stringent regulations were put into force in Germany with regard to the arrangements in match-factories, especial stress being laid upon the efficient ventilation of the separate rooms in which the operations of mixing the igniting compositions, dipping, drying, and removal of the splints from the dipping frames, were to be conducted. Finally, in 1906, Germany adopted absolute prohibition of the use of white phosphorus (*see post*, p. 235)

In Denmark and Switzerland, the use of matches containing ordinary phosphorus was forbidden in 1875 and 1879 respectively; and only the so-called Swedish safety matches have been permitted to be used in Denmark since 1875.

Between 1879 and 1882 the use of matches free from phosphorus and inflammable on any surface was allowed in Switzerland; but a committee appointed by the Department of Commerce found that these matches were unreliable and often dangerous: in 1882 the Swiss Government passed an Act, prohibiting the use of any but safety matches: and in 1906 Switzerland was one of the high contracting parties to the international treaty for enforcement of the total prohibition of poisonous phosphorus.

For methods of detecting white phosphorus in match compositions, *see* Thorpe, Chem. Soc. Trans. 1909, 95, 440; Schröder, Arbeit. Kaiser. Gesand. 1913, 44, 1; Analyst, 1913, 289.

Efforts were early made to use red phosphorus, discovered by v. Schrötter in 1845; and G. E. Pasch, in 1844, took out a patent for a red phosphorus-product, which he believed to be an oxide of the element; and he is by some authorities regarded as the pioneer in the utilisation of red phosphorus. It is claimed for him that he discovered that a striking surface containing this substance could be used for matches free from phosphorus. Matches tipped with compositions prepared with red phosphorus were manufactured in Germany in 1850, in England (by Dixon & Co., and Bell & Black), Austria (Fürth, of Schüttenhofen, and Foster & Wawra, Vienna), and France (Coignet & Co., Paris), in 1851: but they were not successful; and, although improved matches of this description were patented by Albright, of Birmingham, in 1856, and were again to be seen at Paris in 1867, and Vienna in 1873, they did not come into general use. The higher cost of red phosphorus had much to do with this; but, in addition, the mixtures used were unstable and dangerous. Some of the earlier igniting compositions made with red phosphorus undoubtedly contained excessive proportions of the element. Of late years, matches of very fair quality have been produced, with far lower percentages; and there are upon the market at the present time various red phosphorus matches, some of which have been analysed by the writer. Many inventors of late years have proposed methods of diminishing the violence of the reaction between this variety of phosphorus and potassium chlorate, of lowering the ignition temperature of mixtures containing red phosphorus, or of rendering matches made with it less absorbent of moisture; such as previously mixing it with zinc (Simonet, 1893) or with sulphur (Bals and Gurowitz, 1896); substituting calcium plumbate for the potassium chlorate in red phosphorus compositions (Schwiening, 1896); adding chalk, &c. (Cordes, 1898); coating the red phosphorus with paraffin wax or some other suitable hydrocarbon (Akester, 1899, and Thompson, 1899); associating it with a borate or a phosphate (Säfström, 1901); boiling in aqueous solutions of various metallic salts (Purgotti, 1902); admixture with cork and flour (Bokmayer and Swoboda, 1905); or with zinc oxide and chalk (Chem. Fab. Griesheim Elektron, 1909). Schwiening's composition was adopted by the German Government, in consequence of the weighty objections to the use of ordinary phosphorus. The calcium plumbate apparently retards the explosion of the red phosphorus and chlorate mixture, thus moderating the violence of the combustion; but the matches have been subjected to somewhat severe and general criticism, on various grounds.

The Société Caussemille Jeune & Cie and Roche & Cie in 1909 proposed the treatment of red phosphorus by distillation and filtration, for the purpose of purifying it from acidity and alkalinity. The product they termed 'neutral amorphous phosphorus.'

In 1855 Lundstrom, of Jönköping, Sweden, acting on Bottger's suggestion, that friction matches might be so made as to be capable of igniting only on an especially prepared surface, manufactured the first true '*safety matches*,' by putting the oxidising mixture on the match-sticks and red phosphorus on the *box*. Such matches ignited only when rubbed on the specially prepared surface, or 'rubber,' on the side of the box. Lundstrom's process was patented in England in 1855 by F. May, of Bryant and May, and since that date 'patent safety matches' have been largely and increasingly manufactured in Great Britain. Matches on the same principle were made, soon after Lundstrom's invention, by Coignet & Co., by Furth, of Schüttenhofen, and other continental manufacturers. In the 'allumettes androgynes' of Bombes Devilliers and Dalemagne (1859), the red phosphorus composition was at one end of the splint and the potassium chlorate at the other. The splints were broken, and the ends rubbed together. Field (1882) adopted a similar plan. The Swedish safety matches, so largely imported into this country, are on Lundström's principle. There have been comparatively few attempts to improve upon the safety match. Herz (1894) and Thimann (1894) worked in this direction. Viebig (1895) proposed to coat the heads of safety matches with a layer of the rubbing composition, or with a 'strike-anywhere' paste; and Craveri (1897), also Engl (1903), described safety compositions and rubbing surfaces therefor. It is common knowledge that some safety matches can be ignited, without the aid of an especial rubber, by friction—with a swift, sweeping movement—against a smooth, even surface, such as glass, polished oak or ebony, slate, &c.

A further step was taken in 1857 by Canouil, and by Hochstätter, of Darmstadt, in the production of '*non-poisonous safety matches*,' neither the igniting nor the friction compositions of which contained any variety of phosphorus. In Hochstätter's matches the oxygen compounds used were potassium chlorate, potassium dichromate, lead dioxide, &c., and the phosphorus was replaced by a mixture of antimony oxysulphide and flowers of sulphur. The oxidisable ingredients of Canouil's compositions, where stated, consisted of sulphur, iron pyrites, and various cyanogen compounds of lead. It is probable that some of the earlier so-called non-phosphoric matches were not altogether free from phosphorus. Vaudaux and Paignon improved upon Canouil's formulæ; and other compositions for non-phosphoric matches were those of Lutz (1858) and Kummer and Günther (Königswalde, Saxony, 1861). Schnell (London, 1861), Palmer (London, 1868), and others used lead thiosulphate, recommended by Wiederhold in 1861. Mayer (1865), C. Liebig, and Palmer (1869), also produced friction matches, containing, respectively, antimony sulphide and lead cyanide (Mayer), antimony sulphide and nitromannite (Liebig), and iron thiosulphate (Palmer), in place of lead thiosulphate. Jettel, in 1869, suggested the use of basic lead picrate. (Wiederhold had already tried potassium picrate.) Later, in 1879, L. Wagner, of Mühlheim, patented a match containing lead thiosulphate, antimony sulphide, sulphur, and finely powdered charcoal. Again, in 1881 and 1884, Schwarz, of Gratz, patented compositions containing lead thiocyanate, and lead sulphide in place—partly or entirely—of antimony sulphide. Among other substances proposed as ingredients of non-phosphoric safety match compositions are the thiosulphates of copper and sodium (R. Peltzer); copper thiocyanate, lead chlorate, finely divided metallic sodium (Fleck, 1868); and barium chromate (Garber, 1888).

Most of the compositions for non-phosphoric matches have been described by their inventors as 'ignitable by friction on *ordinary* surfaces'; in some instances, however, a special rubber was necessary. Many of the earlier non-phosphoric friction matches inflamed on ordinary surfaces with great difficulty; others ignited with almost explosive violence, and most were very hygroscopic. The vapours of lead, cyanogen, and thiocyanogen compounds, evolved during the manufacture and ignition of such matches, were probably in some cases injurious.

The more notable compositions for non-phosphoric 'strike-anywhere' matches, as now made, will next be described.

Among the various substitutes for white phosphorus, used of late years in strike-anywhere matches, phosphorus sesquisulphide undoubtedly holds the first place. Discovered by G. Lemoine in 1864, this compound was introduced in 1898 for match manufacturing purposes by H. Sévène and E. D. Cahen, of Paris. Having regard to present conditions, it is, in the opinion of practical match-makers whom the writer has questioned on the subject, unquestionably the best substitute for ordinary phosphorus so far discovered. It is non-poisonous, yields no injurious vapours during the operations in the factory, is reasonable in price, and the matches made with it are as sensitive as can be desired. Phosphorus sesquisulphide is a yellow powder, soluble in carbon disulphide, and inflames in air at 98°-99°. This compound was at first adopted in 1898 by the French Government; it is used for all strike-anywhere matches manufactured in this country, and is now entirely used in the United States of America.

On the continent also phosphorus sesquisulphide is preferred and used to the exclusion of all other substitutes. Scarlet phosphorus or bright red phosphorus patented in the year 1902 by W. Muir, and C. R. E. Bell—was a competitor to a small extent to sesquisulphide of phosphorus, but has now entirely disappeared and given way to the more efficacious body, viz. sesquisulphide of phosphorus.

Scarlet phosphorus was first prepared by Schenk by boiling a solution of ordinary phosphorus in phosphorus tribromide, and is chemically more active than dark red amorphous phosphorus, and inflames at *circa* 170°, and like phosphorus sesquisulphide is non-poisonous.

Several varieties of light red amorphous phosphorus are in use abroad; and different compounds or derivatives of phosphorus have been patented or suggested—such as metallic hypophosphites (Bohy, Gallay & Co., 1898); hypophosphites in conjunction with chromium trioxide Clayton, 1899); hydrides of phosphorus (Wheelwright, 1906 and 1909; Castiglioni, 1907); combinations of phosphorus with proportions of sulphur differing from that present in sesquisulphide (Wheelwright, 1902; Chem. Fab. Griesheim-Elektron, 1902; Huch, 1903; Gartenmeister, 1908); and the supposed suboxide P_4O (Chem Fab. Greisheim-Elektron, 1903). The last-named company has introduced (D. R. P. 153188, 1902), under the designation 'sulfophosphit,' a product consisting of phosphorus, sulphur, and zinc, very intimately associated together, the basis of the invention being the production of metallic hypothiophosphites and thiophosphites by the union of red phosphorus, sulphur, and metallic sulphides, in theoretical proportions

Besides the foregoing, inventors have proposed the use of lead thiosulphate, associated with calcium sulphide (Braly, 1897), and with potassium dichromate (Gurowitz and Bals, 1898; Trachsel, 1899); copper thiosulphate (Gans, 1898); tin thiosulphate (Jones and Bates, 1898); antimony thiosulphate (Truillet, 1899); copper thiosulphate and 'thiocyanite' (Rosenthal, 1899); cuprous thiocyanate (Puigotti, 1899); and the like. Craveri (1897) suggested the employment of persulphocyanic acid; and a later dipping-composition prepared by Gans (1903) contained 'sulfocuprobariumpolythionate.'

Various materials for the stems have been suggested at different times, such as earthenware, pipeclay, bass, cotton or linen stiffened with chalk and gum (Bell, 1859); bone (Letchford, 1867); cardboard and stiffened calico (Cribb and Rackham, 1874); asbestos (Hynam, 1874); jute and glue in a double wire spiral (Byrt, 1882); wood pulp and paraffin (Molyneux. 1889); compressed peat, turf, or moss (Rosenkütter, 1891; Stiemer and Ziegler, 1892); paper (Farrel, 1890; Bowman, 1893); straw (Castner and Swoboda, 1897); straw, rushes, grasses of various kinds, and the like, dipped in solutions of inflammable substances (Carré, 1908); stems of dried leaves of alfa or esparto (Schaefer, 1906), &c., &c. Fredrikson in 1897 and Lärn (1907) used wooden cores for the stems of wax matches. Craveri (1899) proposed as a composition for the tapers a mixture of ceresin, resin, calcium sulphate, zinc oxide, and potassium nitrate. Steedman (1906) patented waxed stems made from single strips of veneer, with one or more threads applied longitudinally, the whole coated by wax; and the present writer has come across Finnish 'superior patent vestas' (of very poor quality), with stems made in a similar way; obviously the same patented method.

The treatment of the wooden stems has also varied greatly. In the early days of match-making the splints were usually dipped in melted sulphur (v. Romer and others), to ensure ready inflammability of the stems; and hot tallow, resin, and wax were sometimes used for the same purpose. Sulphur-dipping is in this country only of historic interest, but sulphur-coated splints are still to be seen occasionally in matches of the cheapest and worst qualities, mostly of continental manufacture. Of the above named substitutes for sulphur, Bottger (1843) preferred wax, which was also used by Mennons (1857) and others. Later (1861), Letchford introduced the use of melted paraffin or petroleum, also a mixture of paraffin with stearin and Japan wax. Bruce (1863) saturated the stems with potassium nitrate by immersing them in a boiling solution of that salt. In 1891, Bell proposed the use of coloured paraffin. Match-stems have occasionally been impregnated with camphor. In 1867 resin was again applied by Letchford, and Grawitz (1873) used naphthalene instead of sulphur. Mapple (1881) preferred oil or tallow. Paraffin is now almost everywhere used.

Another method of treating the stems is widely adopted at the present time in Great Britain and abroad, especially for safety matches. It consists in impregnating the stems with solutions which have the effect of preventing the wood from burning or remaining red-hot. Stems so prepared become cool almost instantaneously, and do not readily break; there is thus less chance of the heads and fragments of the splints falling and giving rise to fires—a risk commonly present with the thin badly-cut splints (not so treated) of the cheaper sorts of foreign matches. To render the stems uninflammable, solutions of sodium phosphate, sodium tungstate, zinc sulphate, alum, ammonium sulphate, and magnesium sulphate have been used. Field (1879) employed solutions of phosphoric acid, ammonium phosphate, borax and ammonium phosphate together, or boracic acid and ammonium phosphate; Percival (1887) proposed the use of 'cyanite' for the end held in the hand, the body of the match being impregnated with a 'weak gummy varnish' to prevent the embers from falling about; and Louisa A. Thomas (1896) suggested the employment of sodium silicate.

F. Gerken and G. Gohasch (1883) affixed small friction-tablets to the stems, so that when a match was withdrawn from the case its head came in contact with the roughened surface on the stem of an adjacent match, and in this manner was inflamed. The proposals of Galy (1908) and Walsh (1908) were not altogether dissimilar. The last-named inserted the striking composition in a notch in the stem of the match.

Tubes, to hold a single match, have been so constructed that the match on withdrawal is inflamed by friction of the head against striking composition lining one end of the tube. The other end is closed. An allied device is a tube open at both ends, and on finger-pressure being applied to the match-stem projecting at one end, the head of the match is pushed past the striking composition lining the other end; on coming into the air directly afterwards it is inflamed.

To render match-stems waterproof, collodion, resinous varnishes, and caoutchouc solutions have been employed.

Headless matches have been suggested by Simonet (1893), Neuberg (1897), Fog and Kirschner (1898-9), Budde (1900), and Haffner (1907). Matches tipped at both ends were proposed by Scarlett (1891), Aldridge (1899), Potts (1901), and Nicolay (1904). ‘Double-tip’ matches, an important modern invention, are described further on.

The development of the machinery used in match-making has more than kept pace with the improvements in the compositions and in the treatment of the stems. Continuous and automatic machines will be described in the portion of this article devoted to details of the manufacturing operations.

Vestas.- The earliest account of the *wax-taper* as a match stem is in the specification of an English patent taken out by W. Newton in 1832; and, according to Payen, matches of this description were first made in France in 1836 by Savaresse and Merckel, of Paris. Wax, however, in conjunction with colophony, was used in 1832 by Siegel, of Vienna, as an easily inflammable coating (in place of sulphur) for the previously carbonised splints of his oxymuriate matches. In 1862 J. Childs recommended a mixture, of high melting-point, of one part of Carnauba wax with 9 parts of paraffin; in 1866 Letchford substituted jute for cotton in the tapers; and J. G. Gomez and P. Franco (1889) used strips of Bristol board, immersed in a mixture of resin, stearin, zinc-white, &c. Baron (1896) recommended wood-fibre. Hathaway (1897), Scott (1899), Glenister (1907), and others have employed paper in strips or coils. The use in the waxed stems of a wooden core has already been mentioned; and pine-wood sticks are very largely taking the place of wax tapers for this class of match. Wax vestas have been sold in metal cases containing sand-paper so folded that, on the withdrawal of a vesta, its head is inflamed by friction against the sand-paper, the act of withdrawal thus igniting the match.

Fusees, &c.—Cigar lighters—of brown paper, cardboard, German tinder and the like—impregnated with a solution of nitre, often scented, and tipped with various igniting compositions, mostly phosphoric, were made by Siegel (1832, 1835), v. Römer, and others. Of the newer kinds of cigar-lighters, variously known as ‘flaming vesuvians,’ ‘etnas,’ ‘fixed stars,’ ‘braided lights,’ &c., consisting generally of three parts—a stem of wood or glass, a head or ball of ‘pastille’ composition, and a tip of igniting composition—one of the first was described in 1849 by J. Palmer. Grimes (1859) introduced wires into the composition-ends of his splints, to prevent the heads from falling off when pressed against the cigar or pipe. Bell & Black (1859) made the stems of wire, coated with a non-conducting composition, such as gum and whiting, or glue and whiting or flour. Simlic (1862) put the composition on a tube fitted on to the end of the splint, and preferred glass. He also (1863) tried stems of slag and powdered oyster-shell, mixed into a paste and calcined; and wire covered with thread or cotton, dipped in coloured liquid gum. Battcock (1863) made stems of stone and slate; and Barker, in the same year, used pipeclay stems, tipped at each end. Ford (1878) softened the splints by treatment with caustic potash or soda, and then subjected them to the action of a solution containing 10 parts of nitre, 1 part of potassium chlorate, and 1 part of sugar in 12 parts of water: this process of course rendered the wood highly combustible. Methods of treating the wooden stems with alkaline and other solutions were patented by the Aktieselskabet ‘Progress’ (1902), and in the previous year by A. G. Haehre. Evans (1882) rendered the stems of his vesuvians incombustible, by the use either of asbestos paint or of sodium tungstate solution. The invention of A. Hill (1904) was similar. G. A. Sweetser (1884) formed his stems of plastic material moulded into the required shape and size round a core. In the ‘braided’ lights, still manufactured to a small extent by Bryant & May, and J. Palmer & Son, the composition is retained in position by pieces of thin wire, over which strands of cotton are twisted by the braiding machine. T. J. Clanchy, in 1868, obtained provisional protection for a combined match and fusee, consisting of a shaft or stem with a fusee-head at one end and a match-head at the other. In 1885 R. Bell, proceeding on closely similar lines, introduced the ‘fusee vestas,’ or wax-stemmed vesuvians, in which the essential parts of a vesuvian are present, but the stem was of jute, hemp, flax, cotton, or a mixture of some of these fibres, coated with paraffin, wax, or stearin. According to another patent of the same year, this inventor introduced a wire core into the stems; and in 1886, C. R. E. Bell devised a hollow cylinder or bead of combustible material, to be sold separately, for application to a match or vesta, for use in a light wind. J. J. Williams (1895) had a somewhat similar idea. Salts of strontium and barium have sometimes been introduced into the compositions of vesuvians, to cause them to burn with coloured flames.

Vesuvians have been almost entirely superseded in this country by vestas with pine-wood stems (such as the ‘Swan’ vestas, introduced by Bryant & May), and in America by the ‘double-tip’ match, invented in 1905 by the Saginaw Match Company. There is also a considerable production of matches with cardboard stems, somewhat upon the lines of the earlier ‘fusees.’ The ‘book-matches,’ made by Bryant & May, are of this type; two layers, stitched together, of flat, cardboard-stemmed matches, united by the base, are contained in a thin pasteboard case, with a red phosphorus striking surface on the exterior. These matches are of the safety class.

Repeating or continuous matches have been invented, but have never had much sale. The earliest English patent of this kind was that of Dove (1862), in which the igniting composition was attached at intervals to a continuous band or strip of material, inclosed in a box. Later devices of similar nature were those of Tylor (1865); Rogers (1869); Perkins (1869), who mixed the igniting composition with collodion, a strip so composed fitting into a case like a pencil case, from which it could be withdrawn at will; Samuel (1871); Jonas (agent, Pollet, 1878); and Klein, same year.

Cigar-lighting appliances of a special kind. Many instantaneous igniters, not matches, have been invented for the convenience of smokers. These contrivances, though numerous, have not interfered with the steady development and increase of the match industry; and a few types only of such inventions will be mentioned. Among the earliest were the 'D'Bleaml'n Cigarrenzunder,' cigar-lighters, made by Pollak, of Vienna. This appliance consisted of a small, nitre-steeped, variously coloured, artificial flower, the stalk of which was inserted in a cigar. A little boss of igniting composition in the centre of the flower was inflamed by friction. An alloy of the metals sodium and potassium has been used. A small quantity of the alloy is withdrawn from a case or tube by a wire, which is then rubbed across and ignites a charred wick (1887 and 1888). Another appliance is simply a pocket edition of the old flint, steel, and tinder-box. A fourth device (W. D. Borland, 1889) is an attachment to cigars or cigarettes, by which they are easily lighted, even in a high wind. A minute portion of nitrocellulose fabric, forming a ring round the cigarette, is inserted under the paper, and on applying a spark the material takes fire and slowly smoulders until the whole end is glowing.

Automatic igniters in which is used an alloy of cerium are now extensively sold in France, and to a smaller extent in this country.

Statistics and Legislation. According to the Census of Production, 1912, the total value of the output of matches of all kinds including wax tapers, vesuvians, braided lights, &c., of British manufacture was in that year £783,183. The value of the exports of matches of the United Kingdom manufacture amounted in the same year to £110,000, or about one-seventh of the output. The annual output of one British company alone is at present not less than 8,000,000 gross of boxes, each box containing on an average 60 matches, or a total annual output of 480,000,000 matches.

The total value of the materials used in the production of matches of British manufacture was in 1912 £427,281. The consumption in Great Britain and Ireland of all matches in 1912 amounted to about 20,000,000 gross of boxes. Safety matches continue to increase in popularity, whereas in 1899 about 18 p.c. of the matches consumed were safety, and 82 p.c. strike-anywhere, in 1912 the proportions were about 40 p.c. safety and 60 p.c. strike-anywhere. Vesuvians are almost obsolete, but *small* quantities of braided lights and flaming vesuvians are still made Swan vestas, with pine-wood stems, introduced by Bryant & May, have virtually supplanted vesuvians, and have considerably reduced the consumption of wax vestas.

The value of all matches (British and foreign together) consumed in Great Britain and Ireland in 1912 was computed at £1,500,000.

Assuming that 20 million gross of boxes, each box containing 60 matches, were so consumed and taking the population of the United Kingdom at 45·2 millions (Census, 1911), this consumption would be equal to 10 matches per head per day of the population.

In the United States of America, there are said to be manufactured 310,250 million matches per annum. Assuming a census of 85 millions this is equivalent to nearly 10 matches a day *per caput.*

At the present date (June, 1918) there are in Great Britain and Ireland seventeen match factories. By far the largest and the most modern are those of Bryant & May, Limited, at Liverpool and Bow, London, E

At the present time (May, 1918), owing to onditions brought about by the war, the consumption of matches in the United Kingdom is considerably restricted. The import of foreign matches having been prohibited owing to shipping difficulties, present supplies are restricted to about one-half of the normal.

Owing to the increase in the value of raw materials as well as owing to the introduction for revenue purposes of a match tax, there has been an enormous rise in the value of matches. The tax introduced in the year 1916 amounted to 3s. 4*d.* per 10,000 matches, or on a gross of boxes, each box containing 60 matches, 2s. 10½*d.* per gross, the tax being more than the total value of the matches under pre-war conditions.

This tax has again been increased, and this year (1918) amounts to 5s. per 10,000 matches. It is estimated that the tax at the latter figure will yield a sum equal to £2,000,000 to the exchequer annually.

It will be interesting to recall that this is not the first occasion when an attempt to tax matches was made, but the strenuous opposition of the manufacturers and workpeople combined compelled the then Chancellor of the Exchequer, Mr. Robert Lowe, to relinquish the idea; and since that time there had been no further attempts to tax matches until the present tax was introduced when manufacturers and workpeople patriotically assisted to make it a success.

In Russia there are or were 49 factories, in Sweden 10, in Norway 2, in Belgium 14, in Germany 75, in Austria-Hungary (originally the chief centre of the European match industry) 10, and in France 7. The most important Swedish factories are those of the Jönköpings och Vulcans Tandsticksfabriks Aktiebolag, at Jönköping and Tidaholm, Uddevalla, Wenersborg and Anneberg, and these may be regarded as among the best-equipped of European match works. Among the principal German factories are those of Stahl & Nölke, at Cassel and Kostheim a./M., the Deutsche Zundholzfabriks Aktien-Gesellschaft, at Lauenburg-Rheinau Baden and Vordamm, of the 'Union' Aktiengesellschaft, at Augsburg and Habelschwerdt, Ulm, Göppingen, and elsewhere. The French factories, which are under the direct control and supervision of the Government, the manufacture of matches having been a State monopoly since 1890, are at Pantin and Aubervilliers (both near Paris), Marseilles, Bégles (Bordeaux), Aix-en-Provence, Saintines (Oise), and Trélazé (Angers). In the United States there are 19 companies and firms and 16 factories, including the Diamond Match Company's five works in New York, Michigan, Ohio, California, and Wisconsin. The Diamond Match Company is by far the largest and most influential American company, and its output is probably about 75 p.c. of the entire production.

By the international treaty of Berne, 1906, most of the countries of Europe have bound themselves to enforce within their territories the prohibition of the use of white or yellow phosphorus. The importation and sale of matches containing ordinary phosphorus are entirely prohibited in Great Britain and her Crown colonies (since 1908); in Germany, France and her colonies, Austria, the Netherlands and the Dutch Indies, Luxemburg, Finland, Italy, Spain, and Switzerland (since 1906); and in Denmark (since 1875). In Australia the importation is forbidden. Since January 1, 1912, similar prohibition has been enforced in Canada. In Norway and Sweden, the use of white or yellow phosphorus is forbidden in the manufacture of matches for home consumption, but not in making matches for export trade. As the outcome of the Conferences at Berne, in 1905 and 1906, of representatives of most European Governments, the British Legislature on Dec. 21, 1908, passed the 'White Phosphorus Matches Prohibition Act' (8 Edward VII., 1908, ch. 42), which has been in operation since January 1, 1910. With practically no exception all civilised countries have prohibited the use of yellow phosphorus in the manufacture of matches, and where this has not been accomplished very stringent regulations have been put in force, making the use of yellow phosphorus very inconvenient and difficult to manufacturers. The United States passed a prohibition Act (January 1, 1911), and yellow phosphorus for match making is now a thing of the past in that country. The stringent regulations in European countries previous to the entire prohibition of yellow phosphorus kept down the quantity used to 6 or 7 p.c. (Denmark 10 p.c.). American manufacturers prior to prohibition were said to be using 14 to 20 p.c. The humidity and warmth of the American climate increased the danger to the workers. The extremely sensitive double-tip match recently introduced in America contained quite 20 p.c. yellow phosphorus. This double-tip match is now made with sesquisulphide of phosphorus.

The President of the United States recommended the imposition of a heavy Federal tax in order to discourage the use of white phosphorus, and the Diamond Match Company have voluntarily surrendered their patent rights for the use of tetraphosphorus trisulphide, so that any match manufacturer in the United States is free to use this compound.

Great Britain's exports of matches to foreign countries are smaller than formerly, and her Colonial trade has diminished owing to the establishment of factories in the colonies themselves, notably by Bryant & May, Bell & Co., in Australia and New Zealand, and the Lion Match Company in South Africa. Notwithstanding excessive competition, the home trade is, nevertheless, very large.

As regards the quantities of phosphorus used in the match industry, there are not at the present time any figures available. Probably about 40–50 tons per annum were used in the British Isles over the 15 years prior to 1890.

MANUFACTURE.

Probably the best way of conveying an idea of twentieth-century methods of manufacturing matches will be to begin by describing the operations as they are conducted in the most extensive and modern match works in this country—the factories in London and Liverpool of Bryant & May, Limited, who are, as already stated, the largest British makers, and among the largest in the world. The operations so described may be regarded as typical of the work as now carried on under the latest and most advantageous conditions. Some account will then be given of the manufacture as conducted upon a smaller scale, and of the more noteworthy differences and modifications in the machinery used, or processes followed, in other British, and—so far as space permits—in the more important foreign, match works.

The manufacture may be considered under the following heads: (1) *Ordinary matches*:—the nature of the wood used; making the match-sticks or splints, and boxes; making and packing the matches; (2) *Wax matches*:—making the tapers; making and packing the matches; (3) *Safety matches*; (4) *Vesuvians*, (5) '*book-matches*,' and (6) '*double-tip*' matches.

1. **Ordinary matches.** *Nature of the wood used.*—There is considerable variety in this. Pine, aspen, spruce, fir, poplar, lime, willow, and beech-wood are used. Alder- and cedar-wood have also been employed. Aspen, and poplar-woods are imported into this country mostly from Russia (Riga, Libau, Windau, and Petrograd); pine, spruce, and fir from Canada and the United States of America. There is an increasing scarcity of timber, especially of pine-wood. For British matches, the splints formerly were chiefly, and still are largely, manufactured from pine-wood: aspen, poplar, and other woods have long been used for this purpose by continental makers. Aspen-wood for match manufacturers' requirements must be free from pith and knots; and stems from 10 to 20 inches in diameter are the most serviceable. Rafted aspen is less satisfactory than unrafted. Spruce-wood is employed for the packing cases, planed and dovetailed boards for which are imported into this country.

Making the boxes and splints.—Although some of the smaller match-makers, here and in parts of the Continent, still use boxes made, or put together, by workpeople in their homes, a highly important and prominent department in the leading manufactories of Great Britain, America, and continental Europe, is that devoted to match-box making by machinery. The operations, both for box-making and splint-cutting, begin with 'cross-cutting,' by a circular saw, of the 7-feet long aspen-logs into 26-inch lengths. These are barked by hand, taken to the '*log-peeling-*' or '*skillet-*' (*squelette*) *room*, *and placed in a species of lathe, the* '*peeling-*' or *veneer-cutting* machine (*Fig.* 1), in which they

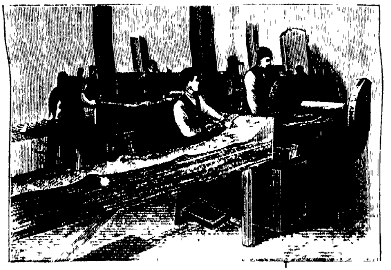


FIG. 1.

Log-peeling or veneer-cutting machine

revolve against a horizontal planing knife acting upon the entire length of the log. A veneer is thus cut from the log, as wide as the rotating wood is long, and of a thickness which depends upon circumstances.

(*a*) *Splints.*—If the veneers be required for the production of splints, the machine is adjusted so that they are the thickness of the splint required—usually from 2·2 to 2·4 mm. for the ordinary small match: if the thinner veneers, used for wooden match-boxes, are desired, the thickness is about $\frac{18}{1000}$ of an inch. Cutters, placed slightly above the planing knife, divide the veneers into narrow bands (—the length of a match), or wider bands (for box-work), as required. In the former case, the narrow bands, divided into convenient lengths and superimposed into piles of 70 or 80 veneers together, are passed under an alternately rising and falling knife, in a guillotine machine, which cuts them into square or rectangular splints. These fall into a hopper, from which by a cyclone fan they are blown along a pipe into another building, where they are 'impregnated' with an acid ammonium phosphate solution and then dried in revolving cylinders heated by steam radiators. Next, they are cycloned back to the peeling-room, where they are 'cleaned' in a '*splint-cleaning*' machine, 'straightened' in a '*straightening*' machine, and packed in trays ready to be fed to the *match-machine*. During both the cleaning and straightening operations, the splints are subjected to a 'jogging' or oscillating motion. This description of splint-making applies only to the rectangular splints, of aspen and similar woods. The stouter and longer square match-sticks, used for the large ordinary and safety matches, are often cut from Canadian pine-wood. The blocks are sawn from a deal, and fed into the hopper of a machine which cuts by means of lancets set horizontally, instead of vertically. These splints, after impregnation, are dried by drying-chamber process. There are two other kinds of wooden match-splints: round-sticks and grooved-sticks. But as these are cut actually in the match machines, an account of the process will be given when those machines are described.

(*b*) *Boxes.*—The thin veneers, intended for the boxes, are wider than those for splints, but they are produced by the peeling-machines in the manner already detailed, the wood being simultaneously scored in readiness to be folded by the box-making machine. They are then guillotined into sizes suitable for the insides and covers of boxes. The skillets for the 'cases,' 'covers,' 'outers,' or (as they are sometimes uneuphoniously called in America) '*shucks*,' are next folded up, pasted and labelled by '*outer*' box-machines, of which there is a row on each side of an endless band or conveyer, carrying the box-covers onwards to a drying chamber. The 'inners,' or drawers of the boxes, are made by machines (Lundgren's patent), which fold up the skillets, paste, and paper-coat the drawers, and similarly feed them on to a carrier, by which they are transported to a drying chamber. Fig. 2 shows some of the box-making machines.

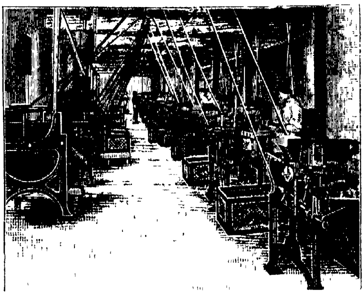


FIG. 2

Wooden box-making machines.

The next step is the application of sand to the 'outers' by the 'sanding-machine' or '*sander*.' The 'inners' are put into the 'outers' by a machine called in the works a '*nester*.' In one room of one of the factories there are about 120 wooden-box machines. Thicker skillets are by some manufacturers used for vesta boxes, and these are cut from spruce-wood by an ordinary

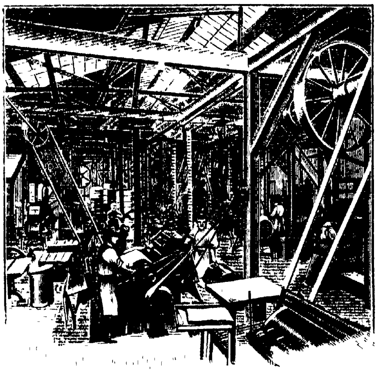


FIG. 3.

Cardboard box-room

'flaking' machine (Day's): but spruce is becoming scarce, and will probably be discarded for the purpose.

Cardboard box-making.—The 'outers' of some strawboard boxes are made by a machine which cuts and scores the cardboard for folding, pastes, and folds it into the form of a flattened tube, prints it above and beneath, glues and sands one side, cuts off the proper lengths, and ejects the finished cases at the rate of 1000 per minute. The insides are made by an equally ingenious machine which cuts out the pieces of cardboard, scores, folds up, glues the ends, and conveys the completed 'inners' in links of a travelling chain until they are dry and ready for filling. A cardboard box-room is shown in Fig. 3. In one room at Liverpool there are 150 cardboard box-machines. The 'inners,' of chip-wood, are machine-made, as above described.

Metal box making.—The metal match-boxes used for 'knapsack' matches are made at Liverpool by a machine invented by Carbone.

The Manufacture of Wooden Matches.

A. By continuous and automatic machinery. In one form of match machine, used by Messrs. Bryant & May, the ready-cut square splints are fed into a hopper near the front of the machine, 'jogged,' and pushed by plungers into apertures in the iron match-plates, or carrier-plates, composing an endless chain about 700 feet long. The chain conveys the splints in enormous numbers, tips downwards, over a hot plate, then through a steam heated bath of melted paraffin wax (m.p. 102°-105°F.), temperature c. 220°F., next over the dipping-roller, which revolves in a trough or vat charged with the match composition, and finally over a great series of drums or carrier-wheels. The period occupied by this is about an hour, and during the passage over the carrier-wheels the matches are dried by the currents of air to which they are freely exposed. There are 100 matches in each row on a match-plate. Having traversed the carrier-wheels, the dry and finished matches arrive near the starting-point, are ejected by plungers from the holes in the match-plates, and are filled into boxes by a '*box-filling* machine,' manufactured by the Diamond Match Company. This machine neatly and regularly deposits the matches in the drawers or insides of the boxes (to which a shaking motion is given, so that the drawers become filled, and there are no spaces left); sheaths the drawers in the covers; and passes the completed boxes along an endless band to *packing* or *wrapping* machine (Lundgren's patent), by which they are put in the familiar 'dozen-packets.' Eight girls attend to a match machine; and the daily output of one machine is 1000 gross of boxes, averaging about 60 matches to a box = 8,640,000 matches *per diem*. The machinery is continuous in its production, and automatic, from the feeding in of the match-sticks to the wrapping of the dozen-packets, which girls put up into gross parcels by hand. The gross parcels are packed in cases, which are nailed together at the factories by an automatic nailing machine (W. S. Doig's patent).

The machines so far described yield square matches. But Messrs. Bryant & May use other match machines, also continuous and automatic, called *grooved-stick* machines. These yield matches with pine-wood stems, nearly circular, but scored longitudinally by two grooves, so that the stems are of the section shown in the figure (Fig. 4). A machine of this kind cuts its own match-sticks from pine blocks, 1⅞ inches deep, fed in horizontally, but at an angle of 17° with the front of the machine. The match sticks are cut from the blocks by dies which act on the downward stroke, leaving the splints sticking up, to be grasped by their upper ends in the apertures of carrier-plates composing a conveyer-chain, just as in the machines last described. The match sticks, bristling from the under surface of the endless chain, pass successively over a hot plate, paraffin-bath, dipping-roller, and series of carrier-wheels, returning to the forepart of the machine, where the finished matches are discharged, and filled into the drawers or 'inners' of cardboard boxes fed to the filling apparatus by hand. Thence the filled drawers are passed along in a continuous stream to a revolving circular table, where sit six or eight girls to receive and sheath them in the cases. Fifteen workers attend to a machine, including wrappers, and each machine produces 800 gross of boxes of matches (averaging 55 matches to a box) in a day of ten hours. The yield of matches per minute may be estimated at 12,000. One girl can feed the machine with 106 boxes a minute, or nearly two boxes a second. From the splint-cutting station of this match machine an exhaust fan draws out wood-dust and imperfect sticks, and conveys them by a pipe to the boiler-house.

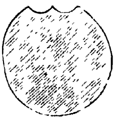


Fig. 4.

Section of a 'grooved stick.'

The *round-stick* machines, which produce the circular-stemmed, pine-wood 'Swan' vestas, punch out round splints, but are constructed similarly to, and upon just the same principles as, the grooved-stick machines. Blocks of pine-wood are fed in; finished matches come out, and are automatically filled into the 'inners,' the final operations of 'boxing' being performed by eight girls stationed at a revolving circular table. Dust and imperfect splints are removed in the manner already described. One of these round-stick machines can turn out about 3,000,000 vestas *per diem*.

Larger-sized matches.—For the production of the larger-sized strike-anywhere matches and safety matches, with square sticks 2¼ inches long, the continuous and automatic machinery is of exactly the same kind as that used for the matches of 'minik' size, with sticks 1⅞ inches long. The splints are fed into the receptacle or hopper of the machine, and the finished matches are deposited in the drawers of the boxes by the filling apparatus previously mentioned. The drawers pass along a channel on to a circular table, where the cases or covers are put on by hand. The productive capacity of one of these machines may be estimated at 6,960,000 matches per day of ten hours. [v. Amer. Pat. 389435, 1888 (E. B. Beecher); and Eng. Pats. 20786, 1894 (E. B. Beecher and J. P. Wright); 17022, 1896 (J. P. Wright).]

Fig. 5 gives an idea of the general appearance of a match machine; Fig. 6 shows one of the machines at first installed, in greater detail and on a larger scale; and Fig. 7 shows a machine room with its range of automatic machines.

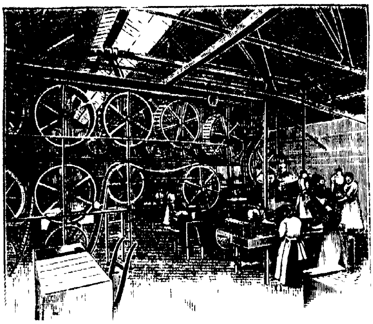


FIG. 5

A match machine.

The adoption of automatic machinery has wrought so great a change in most of the operations of match making, in the conditions under which they are performed, and in the rate and amount of the output, that to describe the present mode of manufacture is virtually to relate the particulars of a new industry. The advantages of the automatic machinery, with the continuous system of manufacture, are enormous. Production is greater, with less labour, than in former days; and the operations are immeasurably more healthy for those engaged. It is scarcely an exaggeration to state that hand labour has been almost entirely eliminated from the actual manufacturing processes. Three or four workers now produce as much as 15 or 20 under the old conditions.

Examples of other forms of automatic match machines are Lagerman's machine, used at Jönköping (described on pp. 239–240, and Figs. 9 and 10), and Roller's. The last-named is constructed upon the same general principles as the match machines already described, but it is of smaller dimensions and capacity. This type of machine is used at Messrs. J. Palmer & Son's, Maguire Miller & Co.'s, W. J Morgan & Co.'s, R. Bell & Co.'s, and Paterson & Co.'s, factories. Ready-cut, single-length splints of aspen-wood are fed into the hopper of the machine; pushed into apertures—150 in a row—in an endless chain; paraffined; dipped; dried by passing over a series of drums; discharged or 'racked out,' and filled into the box 'inners.' These are sheathed in the covers by four workers. There are seven girls to a machine.

Besides the match machines described, there are other continuous and automatic machines, of which the 'Ideal,' made and supplied by Messrs. Sebold, of Durlach, Germany, is an example. Several of these machines are used by S. J. Moreland & Sons, of Gloucester.

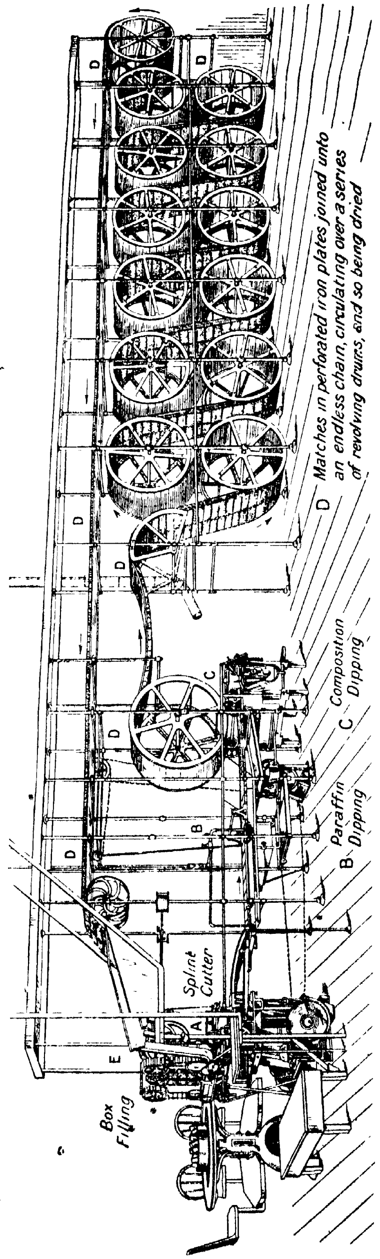

D Matches in perforated iron plates joined unto an endless chain, circulating over a series of revolving drums, and so being dried
C Composition Dipping
B Paraffin Dipping
Splint Cutter
Box Filling
D
D
D
D
D
D
C
B
A
E

FIG. 6.

A match machine.

Preparation of the Dipping Composition.

Almost every maker has his own especial composition and way of preparing it. But the mixtures in use for ordinary matches invariably contain—(1) an *oxidisable body* in a fine state of division, and intimately mixed with (2) *oxidising agents;* (3) *cementing* or *binding materials;* (4) certain chemically *inert bodies* added to increase friction; and (5) *colouring matters.* In strike-anywhere matches, the oxidisable or combustible body in general use is tetraphosphorus trisulphide. Other combustible ingredients are employed, mostly abroad. The more important have been mentioned (pp. 229–232). The oxidising agents principally employed are potassium chlorate, potassium nitrate, lead nitrate, minium, manganese dioxide, and lead peroxide: potassium dichromate, 'oxidised minium' (made by heating minium with nitric acid), ferric oxide, and litharge must also be mentioned. In English matches, potassium chlorate is the customary oxidising agent, used alone or with manganese dioxide, &c. Potassium nitrate is frequently present in continental matches. Glue, gum, gelatin, and dextrin are the binding media mostly used: in Great Britain glue is almost exclusively employed. Very much depends on the quality of the glue, and its drying properties. Powdered glass, chalk, gypsum, and fine sand are among the indifferent bodies added. Prussian blue, ultramarine, smalt, vermilion, chrome yellow, and coal-tar dyes are used to colour the mixtures.

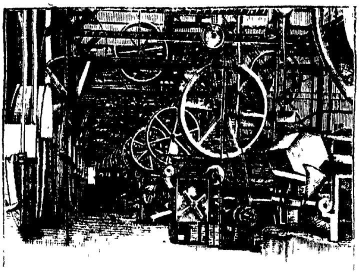


FIG. 7.

A match machine-room.

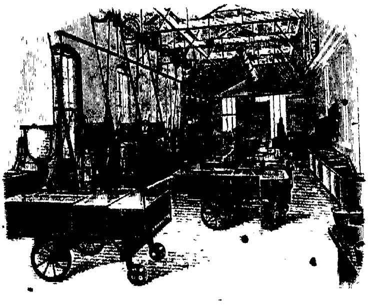


FIG 8.

Composition mixing-room, Liverpool.

Excepting that phosphorus sesquisulphide is now in general use, and that coarsely crushed glue is preferred to glue in large pieces or cakes, there is not much that is new to relate about the operations in the composition mixing-room. There are, of course, numerous minor differences in the methods of mixing the ingredients of an igniting paste; but the guiding principles usually are that the oxidisable body is first mixed with a portion of the inert substances, and with part of the glue or other binding medium, previously dissolved in water, and that the oxidising substance or substances must be mixed separately in another vessel, with the remainder of the glue, &c. Each mixture is passed through a mill, after which the two sections are combined and the whole mass is milled. All quantities are weighed and checked, and proper precautions are taken to avoid 'firing.' Fig. 8 shows a composition mixing-room of the latest type. Some additional particulars, especially with regard to older methods of working, will be found on pp. 231 *et seq.* The other operations, paraffining, dipping, drying, discharging, box-filling, and packing, by automatic machinery, have already been described.

The Manufacture of Matches abroad.

Sweden.—The most important Swedish match manufactories are those belonging to the Jönköpings och Vulcans Tandsticksfabriks Aktiebolag. The Jönköping works of this company are particularly well provided with labour-saving machinery, much of it the invention of the former chief engineer, the late Mr. Alexander Lagerman. These mechanical appliances for saving manual work have been in use for a considerable number of years, and include continuous machinery for paraffining, dipping, drying, and discharging the matches, machines for box-filling, 'sanding' or 'coating' machines, and wrapping machines. The writer is indebted to Chamberlain Berndt Hay, the general manager of the company, for the following particulars of the continuous machines at present in use at Jönköping.

The match sticks, cut and dried, are placed in magazines on the front top of the machine, whence the splints are pushed out into perforated wooden frames, moving upwards on endless chains. The frames, holding the sticks at one-third of their length by means of springs, are brought along, one by one dipped in melted paraffin wax, and then in the strike-anywhere or safety-composition, as the case may be. After passing a 10-metre track, to dry the match heads, the frames return to the front bottom part of the machine, where the matches are discharged, apportioned off, and filled into the empty boxes brought to this part of the machine on a transporting chain, consisting of small iron plates. In Fig. 9 is shown some of the Jönköping machinery. A number of these machines are installed at the older of the two Jönköping factories. Fig. 10 shows one of the box-filling machines used at Jonkoping. The striking-surfaces, whether of sand, emery, glass, or of a red phosphorus composition, are applied to the sides of the boxes by machinery ('sanding' or 'coating' machines); and the finished boxes are mechanically wrapped in parcels of ten or a dozen ('wrapping' machines). One of these machines will pack in a single day, under the *management of two girls, a quarter of a million boxes of matches into finished, labelled 'dozen-*packages,' thus doing the work of 16 or 17 hand-packers.

The Vulcan Factory, at Tidaholm, is a large, well-equipped match-works, where safety matches (chiefly) are now manufactured on a great scale.

Holland. The industry in Holland is of comparatively small dimensions. At Loyens' factory at Breda, a box-filling machine, invented by Paulson, is in use, and is said to be very satisfactory.

Belgium. The principal Belgian factory is that of La Société Caussemille Jne & Cie. et Roche & Cie. (Ghent). Although there have been great improvements in the conditions of the industry, Belgium was behind other countries in regard to match factory legislation prior to the commencement of the late war (July, 1914).

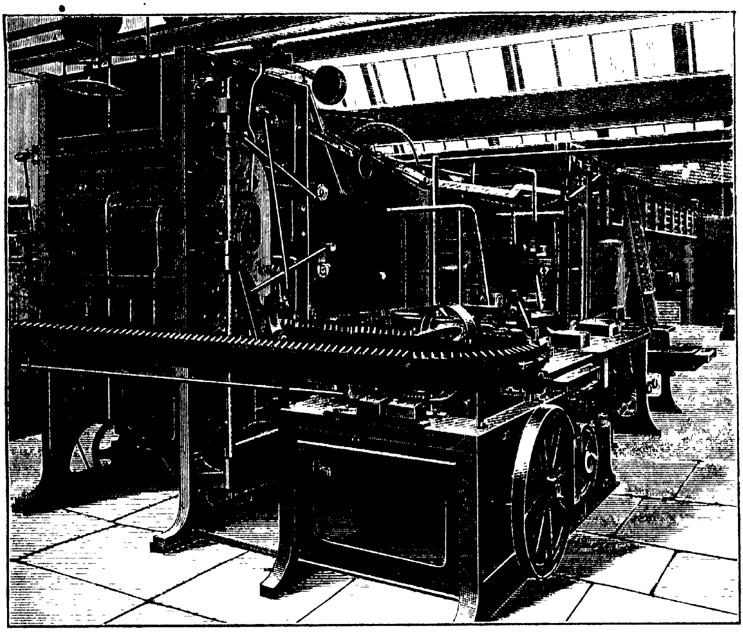


Fig. 9.

Automatic and continuous match machine used at Jonkoping. (Inventor, the late A. Lagerman.)

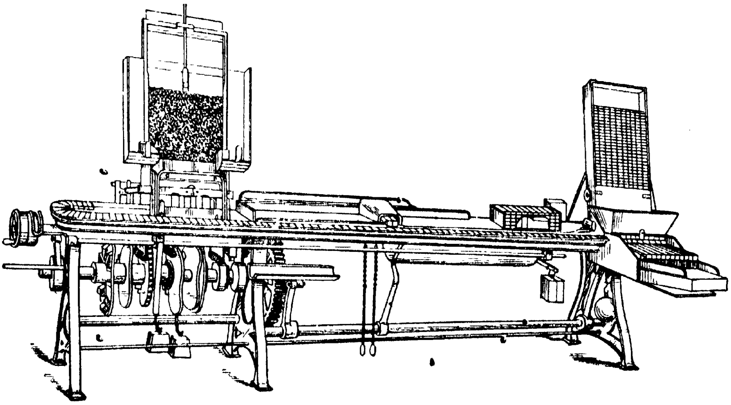


Fig. 10.

Box-filling machine used at Jonkoping. (Lagerman's invention.)

Germany. The match manufacture is of considerable proportions in Germany. The largest German companies, the Deutsche Zundholzfabriks Aktien-Gesellschaft, previously mentioned (p. 234), the Aktien-Gesellschaft für Zundwarenfabrikation Stahl & Nolke, and the Union Company at Augsburg, use aspen-wood for the production of both splints and boxes, the veneers for which are cut in a 'peeling' machine of the usual type 'Inner' and 'outer' machines, like those already described, are employed to make the boxes, into which the dipped matches are filled by a machine, similar in principle to those in use at Jonkoping The productive capacity of the box-filling or 'boxing' machine is such that, under the superintendence of one girl, it will yield 25,000 filled boxes in 10 hours. After filling, the boxes are coated on the two narrow sides with a striking composition, by conveyance on an endless band between two revolving brushes, supplied with the composition by rotating discs. The boxes are next carried through a drying channel 6 metres long; and, finally, a 'packing' or 'wrapping' machine automatically assembles the boxes in series of ten or twelve, wraps these in paper (cut by the machine from a roll, and properly folded), pastes the folded flaps, and labels the package The writer is indebted to the Stahl and Nolke Company for some of the foregoing particulars, and for further information relating to the industry in Germany. Other German manufactories have been referred to on p. 234. One of the principal manufacturers of modern types of match-making machinery is A Roller, of Berlin. A large part of the aspen-wood used in Germany is imported from Russia; some, however, comes from native forests. But there is a growing scarcity.

Austria-Hungary. In Austria-Hungary, probably the most important factory, and certainly one of the oldest, is that of Bernard Furth, at Schuttenhofen, in Bohemia, established in 1838. The founder is stated to have been the first to use red phosphorus as a substitute for white or yellow phosphorus, and in 1854-55 he sent into the market matches with red phosphorus in the rubbing surface on the box--thus adopting a suggestion made by Bottger. These first matches of the safety type were not commercially successful, however, and it was not until in 1855 Lundstrom improved the invention, that the 'safety match' of the present day became a practical match

France. The processes and machinery in use at the two chief State factories in France are here briefly described. In the match factory at Aubervilliers, twenty automatic machines, invented by H. Sévène and E. D. Cahen, are employed. One of these machines, worked by only three operatives, can produce in 10 hours 50,000 boxes of 50 finished matches, or about 15 million boxes per annum. For the same output in the old days twenty workers would have been required The French machinery is constructed upon the same general principles as that already described. Splints, fed into a receptacle by hand, fall from a vibrating hopper into 110 grooves of a horizontal iron plate, to be expelled by a plunger at every stroke of the machine into corresponding grooves of a charger, bridge, or transporting table, having a backward-and-forward motion between the horizontal plate and a vertical part of a long, endless band of carrier plates—the carrier or 'presse.' Each carrier plate is 2½ inches long (in the direction of its journey), 48 inches wide, and is perforated by five rows of equidistant circular holes, 110 in each row. The diameter of an aperture is equal to the side of the square section of a match-stick. When the charger approaches the 'presse,' a plate or 'follower' rises behind the grooves and prevents the sticks from receding. The splints, being longer than the width of the charger, project beyond its edge, and are pushed into the 110 holes of a row in the carrier plate. To prevent bending and breakages of the splints, a horizontal plate presses upon the grooves of the charger, which retreats empty to receive its fresh load. The endless band moves along, bristling with splints, which are carried, over a hot plate, and through a paraffining-bath, secondly, through a sulphur-bath, and thirdly over a rotating grooved cylinder partially immersed in the igniting composition or 'paste.' Thence the conveyer chain travels many yards, for the drying of the matches to be effected; and, finally, at the end of the cycle of operations, plungers expel from the holes the finished matches. These fall, in regulated series, into receptacles, whence pistons fill them into boxes, fed into the machine by an operative, but mechanically opened and shut.

In France, the splints are made of Russian aspen and French willow, the former being preferred. Birch and poplar are used as well. The timber is sawn and cut into splints at Saintines. 'Parlour' and safety matches are largely manufactured at Pantin; wax stems or tapers only at Marseilles.

Norway. The chief match works in Norway is the factory of the Nitedals Tandsticksfabriks, near Christiania. Fig. 11 shows Arehn's box-filling machine (Lundgren's patent) in use at most of the European factories and in many parts of the world.

America. An account has already been given of the present conditions of the industry in the United States of America, and of the Diamond Match Company's machinery, used in the States by that company, as well as in Great Britain by Bryant & May.

Japan. In Japan, a country enjoying at one period a virtual monopoly of the markets in the Far East, there are about 150 factories. Three-fourths of the workers, 25,000 in number, are women. Osaka and Kobé are the centres of the industry. As long ago as 1892 matches ranked fourth among the articles exported from Kobé, and in the following year many new factories were established in Japan, with the result that the output and export of matches enormously increased, and continued to expand until about six years ago. Depression of trade set in, and in 1910 seventeen factories in Kobé and thirteen at Osaka for a while suspended operations, with the result that the output fell off considerably. The most formidable competitors of the Japanese are the Swedish and Austrian manufacturers, who have encroached upon the markets in the Far East. Phosphorus and sulphur matches are manufactured at Osaka; safeties at Kobé. The production of wax matches is almost entirely a household industry.

In the year 1909, the total export of matches from Japan amounted to 41,407,083 gross, valued at £1,186,738. During the first half of 1910 there was a decrease of 40 p.c. in the export as compared with the corresponding period in 1909. There has been an enormous increase in the production in recent years.

China. In 1907 there were three factories *in the Canton district: now there are works in Pekin, Hankow, Tientsin, Shanghai, and other* towns. The largest works are at Hankow with 3600 operatives.

India. Hitherto the match industry has not prospered in the Indian Empire, but it has been pointed out that the natural advantages of the country, such as plentiful timber, cheap labour, and inexpensive water transport, justify a belief that the prospects of success are good, provided that the industry is developed on proper lines. India might ultimately secure some of the considerable trade of the Persian Gulf, at present enjoyed by Sweden.

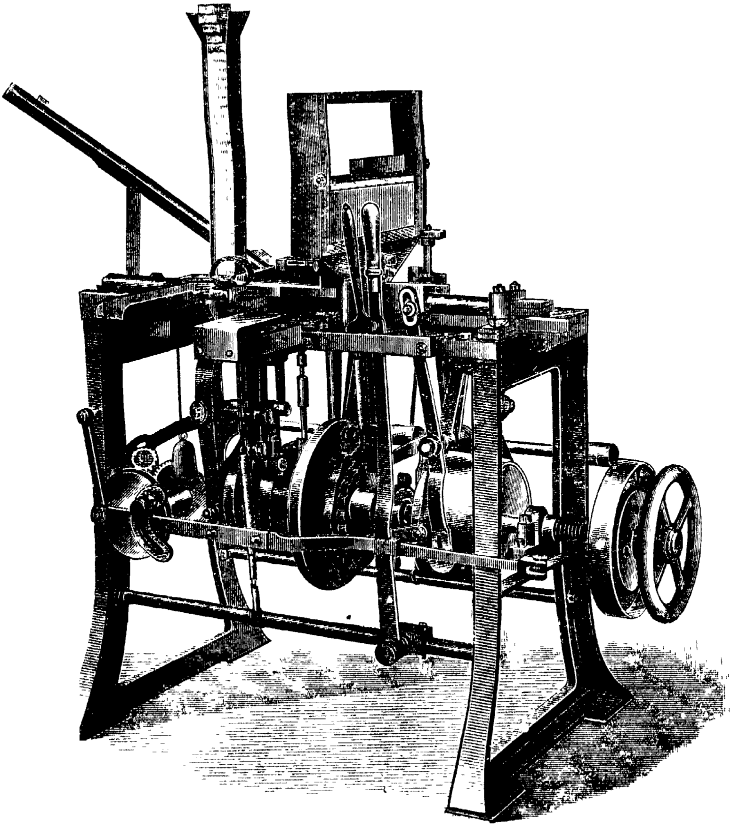


FIG. 11.

Arehn's (Lundgren's patent), box-filling machine.

2. **Wax matches.** The tapers for these are made as follows: from 60 to 100 strands of cotton, of about 20 threads each, are led from a bale, through a measuring machine and guides arranged at a convenient height, into a steam-jacketed tank, containing a mixture of stearin and gum copal or gum dammar, thence through perforations in a draw-plate, and afterwards over a '*drawing drum*' (Fig. 12), 6–10 feet in diameter, revolving on an axis, by hand or steam power (Fig. 13).

From this drum the tapers are led back again through the bath to a similar drum on the opposite side of the tank, and by winding alternately from one drum to the other, they are made to pass 6–7 times through the bath, until the cotton has a coating of fat just sufficient to allow it to pass through holes in a suitable gauge plate. The tapers lastly pass through a perforated hot plate, which imparts a polish to the surface, and are again wound on to a drum, from which they are fed to a 'wax-match machine' of the above-described continuous type. In this machine, patented by the Diamond Match Company, the tapers are cut into stems of the usual length, and inserted in spaces (in which they are held in position by brass springs or clips) in the sections of an endless carrier chain. By this they are conveyed over the dipping roller. Of course, neither the steam-heated plate nor the paraffin-bath is in this case employed. The heads of the wax matches are dried by the journey over the carrier wheels, and the finished matches are automatically filled into the drawers of the boxes. These pass on to a circular table, where girls put them into the covers or outers—just as in the wood-match machines. Some wax matches, however, are filled into the boxes by hand. Each wax-match machine yields about 3 million matches *per diem*. Some manufacturers, Messrs. Palmer & Son, for instance, still use the frame-dipping method for wax matches.

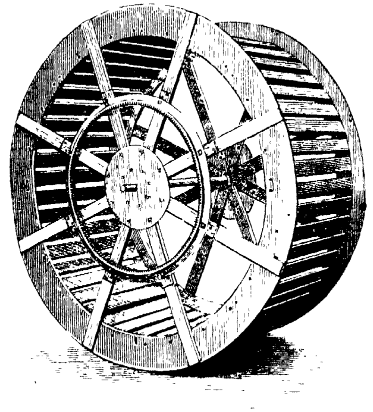


Fig. 12.

A drawing drum.

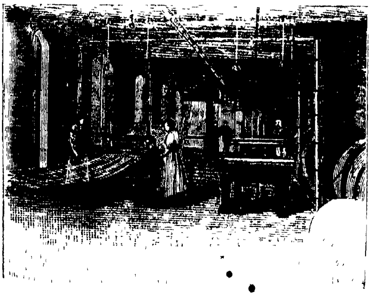


Fig. 13.

Taper-making room.

The taper is then either cut into lengths, which are bundled together and cut into vesta stems by a pivoted knife, the stems being afterwards filled into dipping frames by a small filling machine (Day's) worked by hand or steam, or 60–100 strands of it are wound upon a small drum, and passed from it through guides to a 'cutting and filling' machine of the kind indicated in Fig. 14. In this class of machine the tapers are caused to advance between two feed rollers covered with caoutchouc or other elastic material, and having an intermittent motion, their rotation at each revolution of the driving shaft, or movement of the treadles, being through such an angle as to advance the tapers the required distance under a cutter or cutters working in a vertical plane in front of the feed rollers. The dipping frame (which will hold 6400 stems (80 × 80)) is held immediately in front of a perforated plate through which (when the machine is worked) the cut stems are pushed, so as to rest on a lath of the frame; the frame is now lowered, and the next lath is dropped into position, to receive a row of cut stems, immediately the treadles have been pressed down. When the frame is filled, the stems are dipped, on one side only, in the striking composition. At Messrs. Palmer's factory, the dipped frames of wax matches are dried on shelves in a square chamber, heated by steam pipes, and with a paddle fan in the centre. The 'racking out' is effected by hand.

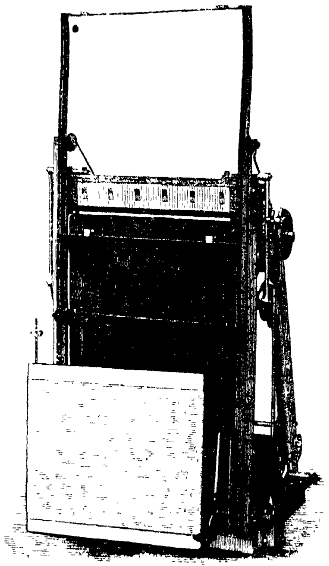


Fig. 14.

Wax-taper cutting and filling machine.

(For wax match machinery, *v.* patents of Beecher and Wright (1895), Hargreaves & Clegg (1896), Pickles (1899), Wiessner (1900), and Harvey (1901).)

3. **Safety matches.** All that has been stated, with regard to the processes of manufacture of ordinary matches, applies to safety matches, excepting the section on dipping compositions. Many more ingredients have been and are used for safety match compositions than are added to ordinary match pastes. So far, safety matches for the most part have been made with red phosphorus in the rubbers only; but

attempts, mostly unsuccessful, have been made to manufacture matches, more or less of the safety type, but without phosphorus, either in the heads or rubbers. The best-known English, Swedish, and other safety matches belong to the first class. The igniting compositions of ordinary safety matches usually contain, as an oxidisable ingredient apart, of course, from the red phosphorus in the rubbers—grey antimony sulphide, with or without sulphur; charcoal, too, is occasionally added. Potassium chlorate, potassium dichromate, and minium are the ordinary sources of oxygen, but manganese dioxide and nitre are also used: glue is the usual binding medium. Colouring matters are seldom added to safety match pastes, which are usually black.

Certain safety matches, made abroad and imported into this country, bearing on their boxes the legend 'Utan swafel och phosphor,' some years since were analysed in the writer's laboratory and found to contain much sulphur.

4. **Vesuvians.** The manufacturing processes for cigar lights, fixed stars, braided lights, and the like, differ little from the methods in use for ordinary matches. The stems, however, are generally of alder or other hard wood (when not of glass, &c.), circular in section, sometimes braided and wired, and shorter than ordinary match sticks. Comparatively few braided lights are now made. Single workers are now employed occasionally in this branch of the industry, which used to engage the services of scores of hands. The dipping frames are smaller, usually filled by hand, and contain from 1600 (40×40) to 2000 short splints, which are dipped at one or both ends. Two distinct compositions are used: the pastille or burning composition, used for the head or ball; and the igniting or striking paste, with which the head is tipped. The pastille composition is a mixture of nitre with charcoal (or coal- or coke-dust), glass-powder, gum or glue, and some scenting ingredient, such as cascarilla bark, satinwood, gum benzoin, lignum vitæ, &c. The stems are dipped more than once in this composition, until the heads are of the required size, and a final dip in any ordinary striking composition is given to the heads after they have been dried. The early 'fusees' (of brown paper or cardboard, impregnated with nitre, tipped with sulphur, &c.) gave place to vesuvians, which in their turn have been largely superseded by wax matches, and these are being supplanted by pine-stemmed vestas. It will be seen in the next section that cardboard stems are at the present time once more used for certain sorts of matches (*cf.* 'book-matches').

5. '**Book**' **matches.** These, in one respect, are an interesting reversion to some of the very earliest types of matches, and to the original 'fusee'; the stems are of cardboard. Two layers of such matches connected together at the base are fastened in a little flat book, the pasteboard covers of which carry a special striking surface. These matches are of the safety type, striking only upon the prepared surface; they are manufactured by machines which automatically print the cardboard, cut it into combs, dip the teeth in the igniting composition, fold up, stitch into books, and affix to the outsides the special striking composition. [*v.* English Patent of Diamond Match Co. (C. H. Palmer, and J. W. Denmead), 21788, 1899.]

6. '**Double-tip**' **matches.** Double-tip matches have been manufactured in some form for many years and the so-called 'Vesuvian,' 'Braided Light,' and 'Flamer,' were all double-tip. More recently, however, this idea has been applied to the ordinary match, and the genesis of the application is perhaps to be found in a proposal of R. and D. Maguire (1898), according to which a large flame-producing head consisting of a composition containing no phosphorus, highly inflammable, but not ignitable by friction, is tipped with a cap composed of a white phosphorus bearing composition readily ignited on any striking surface. The cap which is applied by a second dipping may contain 6 p.c. of white phosphorus (but this, of course, has now been superseded by a composition containing sesquisulphide of phosphorus). Somewhat similar suggestions were those of Lindner (1899), and the Saginaw Match Company (1905). The last-named company, which in America is credited with having originated the double-dip match formerly used for the bulky part of the head, a detonable composition, consisting of an ordinary strike-anywhere 'parlour' match compound, containing about 6⅓ p.c. of white phosphorus, and for the cap or tip a noiseless and non-detonable composition containing no less than 22 parts of white phosphorus. Matches of this character strike with delightful ease on any surface and virtually without noise. But the large quantity of white phosphorus which was present was an obvious objection. The use of white phosphorus for double-tip matches has now, of course, been superseded by the innocuous sesquisulphide of phosphorus, and the caps or tips of the double-tip matches are now entirely made with the latter body; whilst the bulky part of the head is made with a similar composition to that employed on the safety match and is not ignitable by ordinary friction. Double-tip matches have become very popular in America and have to an enormous extent taken the place of the ordinary strike-anywhere 'parlour' matches. In 1909, J. E. State patented a process for producing matches of an allied type, by dipping them successively in a material ignitable by friction, and in a material not so ignitable. The latter is then pushed back by mechanical means, such as a series of rollers, so as to leave exposed a portion of the striking composition at the extreme tip.

The striking surfaces or rubbers. For ordinary matches, mixtures of sand, glass, emery, and the like, with glue or gum, spread on the paper with which the sides of the match-boxes are coated, form convenient friction surfaces; metal gratings, tablets of unglazed porcelain, and porcelain or metal plates with parallel ridges very close together, are frequently employed; and practically any rough or uneven surface—even cloth—can be made to answer. The compositions used in the special rubbing surfaces for safety matches are very various; but the ingredients chiefly present are red phosphorus, antimony sulphide, and powdered glass, made into a paste with glue. The antimony sulphide is sometimes omitted, and manganese dioxide is not infrequently added to safety rubbers.

Among the patents for match striking or rubbing surfaces may be mentioned those of Neuberg (19418, 1897); Craveri (27520, 1897); and Prestwich (23048, 1904).

Older Methods of Manufacture.

The complete process of manufacturing wooden matches formerly comprised the following separate and distinct operations, carried on for the most part, or at all events very largely, by hand labour: 1. 'Scurfing'; 2. Cross-cutting; 3. Steaming; 4. Splint Cutting; 5. Drying the Splints; 6. Filling the Dipping Frames or Coils; 7. Paraffining (originally Sulphuring); 8. Dipping; 9. Drying the dipped splints; 10. 'Laying out,' 'Racking out,' or 'Racking off'; 11. Halving (sometimes also called 'cross-cutting'); 12. 'Boxing'; 13. Packing. It has been shown that nearly all the work can be, and in the more extensive factories is, carried on automatically by continuous machinery; but in some smaller establishments the operations, or most of them, are still performed by the old ways. The three main operations are splint-cutting, dipping, and drying, but a summary of the entire older process will be given.

Splint-cutting. The planks of wood, usually 12–13 feet long, and 3 inches thick by 11 inches wide, were first of all freed from irregularities and roughnesses by the operation called *scurfing*, knives or cutters, rotatory or otherwise, cleaning and smoothing the surface. The planks were then *cross-cut* into blocks or lengths 4$\frac{3}{4}$ inches long × 3 inches thick × 11 inches wide. An ordinary English match-splint, to yield two match-stems, 2$\frac{3}{8}$ inches long, was 4$\frac{3}{4}$ inches long, so that the pieces cut off from the plank, measured in the direction of the grain of the wood, had just the length of a splint. Unless the wood were newly felled, and therefore sappy, these blocks must next be *steamed* (third operation) for about 20 minutes. They were then taken to the *splint-cutting* machine (fourth operation). Very many forms of such machines were invented, but only three kinds were at all generally used in the United Kingdom. The two earlier types of splint-cutting machines were the *toothing* machine and the *flaking* machine. The toothing machine answered well for 'clean' wood, such as pine-wood, but was not adapted for poplar, aspen, &c. The 'vertical flaking' machine is suitable for coarse-grained and even knotty wood, requires little skill in working, and is capable of cutting 650 bundles of splints in a day. The earliest machine belonging to the third class, or combined '*toothing and flaking*' machines, was invented by Tillett (1859). A machine, which for London work to a great extent superseded the foregoing kinds, was Pace and Howard's, and was an improvement upon Tillett's. Some years since, all English and nearly all foreign match-splints were square or rhombic in section. Round splints, such as were yielded by the early machines, were comparatively rarely seen, excepting in Vienna. But at the present time, as has been shown, round-stick matches, such as the pine vestas, and grooved-stick matches, are extensively used. Vesuvians, also, usually are round-stemmed

Splints made from previously separated veneers are now very largely employed, and many of the later machines for splint-cutting have been upon this principle. Some account has been given (*cf.* p. 236) of log-peeling and splint-cutting machines; and this must serve; merely a reference can be made to the numerous patents for splint-cutting appliances taken out during the past 14 years. Some of these inventions relate not only to splint-cutting from veneers or otherwise, but to means of assembling the splints in coils, plates or other holders; also, in certain cases, the splint-cutting is described as the initial stage of a process of continuous manufacture.

The next operation is the *drying of the cut splints.* The splints were formerly always made into *bundles* and then dried. Now they are sometimes thrown loosely into large trays and dried by exposure to warm dry air. (Swedish splints are dried in wire-gauze cylinders revolving within a brick stove.) The dried splints are ready for the operation of *filling the dipping clamps or frames* (sixth operation). Prior to the use of dipping frames, there were the so-called 'bundle-dipped' and 'block-dipped' matches. In the earlier days of match-making, 'dipping-boards' were sometimes employed. 'Frame-' or 'clamp-dipping' was introduced in 1849, and its adoption, which by degrees became general, effected a great saving of time and labour. The dipping clamps are square frames with sides consisting of iron rods, on to which slip laths, each having grooves on its upper surface, and being lined with felt below. The match-splints are firmly held in the grooves by the pressure of the felt. Each frame holds 3900 splints, which, dipped at each end and halved, will yield 7800 matches. The dipping frames were at first filled by hand, but Hynam (1850) and Bell and Grimes (1854) invented machines for the purpose. Improvements followed, and in 1865 Simlick introduced self-acting machinery, driven by steam power, to produce the various movements of these frame-filling machines with greater rapidity and economy of labour.

In 1876, E. B. Beecher, of New Haven, Connecticut, invented machinery to replace frame-dipping, by 'coil'-dipping. This system of working having been introduced into the largest English match-works, effected great and, in many respects, beneficial changes in the method of manufacture; and coil-dipping, where it was adopted, for wooden matches entirely superseded frame-dipping. It is not adapted for the manufacture of vesuvians.

In Beecher's original machine (Eng. Pat. 4293, 1876) the splints were so delivered from a hopper as to be set at regular intervals between the coils of a long flexible tape band, or belt of cotton webbing, about the thickness of a splint, but considerably narrower than its length; this belt was continuously wound upon a short cylinder or drum adapted to a rotating mandril or axis, until a coil, or bundle, or frame, of the desired size was completed. The end of the binding tape was then secured to the preceding coil by a pin or otherwise, the drum and coil of match-splints thus bound upon it being now ready for removal from the mandril for dipping. Being separated from each other by the thickness of the webbing, and by an interval the width of a splint between every two splints, the splints individually received the proper proportion of composition when dipped, and could be conveniently dried in the coil. In an improved form of the machine (1887), Beecher employed an auxiliary or secondary band in connection with the first, for the purpose of holding the match-splints more securely.

The match-splints, having been arranged for dipping in one or other of the ways described, according to the older method now being described, are ready for *paraffining*, or 'the first dipping,' as it is sometimes called (seventh operation). The frames are put on a table, and the splint-ends are levelled, if necessary, by taps with a piece of wood; they are afterwards heated (to facilitate absorption of the paraffin) by application to a hot iron plate, and then immersed in melted paraffin contained in a shallow steam-heated iron tank. Both ends of the splints are thus treated. Sometimes the operation is effected in a brick stove, on the top of which are three shallow, flat-bottomed, square pans, one serving for the preliminary heating of the splint-ends, the second for the paraffining, and the third for the subsequent dipping in the igniting composition.

In all but the most inferior matches, paraffining has entirely superseded treatment with sulphur.

8. **Dipping.** The usual constituents of a match-igniting composition have already been enumerated (pp. 238, 239), and are mixed in the following manner. The glue and potassium chlorate or nitrate are dissolved in warm water, and the phosphorus (assuming that the worker is in a country where it is still legal to use it) is then added to and stirred in the liquid (which should be of a syrupy consistence and at a temperature of about 38°), until a perfect emulsion is obtained The rest of the constituents, powdered glass or sand, colouring matters, and metallic oxides, if present, having been previously 'milled,' are now added, and thoroughly mixed with the emulsion. When, as is now generally the case, a substitute for white phosphorus is used, it is at first intimately mixed with part of the glue solution and inert materials only; the potassium chlorate, with the rest of the ingredients, being added later. The whole is finally put through a mill.

For the operation of dipping, which—in manufacturing upon the older lines—is performed by workmen in a separate apartment called the dipping-room, the emulsion is ladled from a steam-jacketed iron pan on to the dipping plate or table—generally a shallow, flat-topped, iron box, kept hot by steam admitted to its interior. The composition is spread over the plate, and levelled to the required depth by a gauge or 'strickle.' The ends of the splints in the filled frames are then dipped in the thin layer of igniting composition. After the splint-ends have been dipped, the frames are placed in racks to dry.

Dipping by hand, as already described, is most usual in working upon a comparatively small scale; but the igniting composition is sometimes applied by the aid of cylinders or rollers, partly rotating in hot-water jacketed cases, receptacles, or boxes containing the mixture, endless chains conveying the frames or coils over the rollers. And it will have been seen (*ante*, pp. 237, 238) that this system is generally employed in the newer, automatic, and continuous methods of manufacture. Bevelled wheels and other devices (L. Urion, 1856) have also been used for the purpose.

9. **Drying.** The frames of tipped splints are placed on supports or racks, either in the open air or in the drying-room—an apartment maintained during the summer at a suitable temperature by fans or otherwise, and in damp weather and winter kept warm and dry by pipes conveying steam or hot air.

10. **Laying out**; 11. **Halving**; and 12. **Boxing.** The 'headed' and dried splints are next taken out of the frames or coils, as the case may be. The operation is usually termed 'laying out,' 'racking out,' or 'racking off,' and in England is sometimes effected by hand, if the establishment be not very extensive. The nuts and crosspiece at the top of a clamp are removed, and then lath after lath is lifted and the row of double-tipped splints beneath deftly withdrawn. Laying out is also performed mechanically, the machines of Sebold, Schnetzer, and others being used, especially abroad. In the case of coil-dipped splints the process was called 'unwinding,' and differed, of course, materially from the methods applicable to frames. Beecher (1877) invented a machine which simultaneously performs this operation and the next, 'halving,' 'cutting-down,' or 'cross-cutting.'

According to the older method, for frame-dipped matches, handfuls of the laid-out, double-headed splints were divided, 'halved,' or 'cross-cut,' generally by a pivoted or 'lever' cutting knife, and the resulting matches were at once *boxed* (*i.e.* put into boxes) by women, who became exceedingly dexterous in taking up handfuls of splints of just the required number to fill two boxes. The operations of halving and boxing, where white phosphorus was used, caused more loss by 'firing' than any other part of the proceedings in a match factory. It has been mentioned that the loss during boxing or filling is quite trivial under modern working conditions. And, with the continuous manufacture, there is now no halving.

The writer is under obligations to Messrs. Bryant & May, and to Messrs. Bridwell, Hammond, Parrott, Marchant, and Crowther-Beynon for help in the preparation of this article.

E. G. C.

MATÉ *v.* Paraguay tea.

MATECERIC ACID. An acid obtained from the wax of the yerba maté (*Elaeodendron quadrangulatum*) (Reiss.). When the solution obtained by exhausting the leaves of this plant with ether, or better with ether-alcohol, is treated with lime, then filtered and evaporated, a waxy residue is left, which may be freed from chlorophyll by treating its ethereal solution with animal charcoal. This solution, agitated with water to remove caffeine and other substances, and evaporated, leaves the pure waxy matter, which, when boiled with aqueous potash, partly dissolves, leaving a residue soluble in ether, much more butyraceous than the original substance and separable by treatment with alcohol into an insoluble yellow transparent substance, and a soluble portion which is white and melts at 55°. On neutralising with hydrochloric acid, the alkaline solution obtained by saponification of the wax, mateceric acid, is obtained as a white precipitate which has acid properties, and is soluble in ether and in boiling alcohol. It melts at 105°–110°, and has a density of 0·8151 at 26°. From the results of its analysis, it does not appear to belong to the acetic series, but its molecular weight is very high (Arata, Gazz. chim. ital. 1877, 366).

MATEZITE. A saccharine substance obtained by Girard from Madagascar caoutchouc; when treated with hydriodic acid, yields methyl iodide and *matezo-dambose*, an isomeride of glucose. Crystallises in radiating nodules. Rotatory power $[\alpha]_D + 65$; m.p. 187° (Girard, Compt. rend. 77, 995, and 100, 84; Combes, *ibid.* 110, 46).

MATICO CAMPHOR *v.* CAMPHOR.

MATLOCKITE. A lead oxychloride

$$PbCl_2 \cdot PbO$$

of a yellowish colour, found at Cromford, near Matlock, Derbyshire; sp gr. 7·21.

MATRASS. An egg-shaped glass vessel with a narrow neck, used by the older chemists, mainly for sublimations.

MATRINE $C_{15}H_{24}ON_2$. An alkaloid occurring in the roots of *Sophora flavescens* (Ait.). Is a monoacidic tertiary amine. Of the two nitrogen atoms, one forms a lactam ring with a carboxyl group and is changed to an imino-group by hydrolysis with alkali, *matrinic acid* being formed. For its salts and derivatives, *see* Heizaburô Kondô and co-workers, J. Pharm. Soc. Japan, 1921, 659, 1047.

MAURITIUS ELEMI *v.* OLEO-RESINS.

MAUVANILINE $C_{19}H_{17}N_3$. A base isolated by Girard, De Laire, and Chappolot, from the insoluble residues obtained in the manufacture of rosaniline (Zeitsch. Chem. 1867, 236).

MAUVE or **MAUVEÏNE** *v.* AZINES.

MAYNAS RESIN or **CALABA** *v.* RESINS.

MAZOUT. Petroleum residue used as a fuel oil, usually by atomising by a jet of steam after preheating above the flash-point.

MEAD or **HYDROMEL.** An alcoholic drink prepared by the fermentation of honey. Well-made hydromel has a colour between that of champagne and Madeira, is fine in flavour, and contains about 13 p.c. of alcohol.

MEADOW ORE *v.* LIMONITE; also IRON.

MEADOW SAFFRON *v.* COLCHICUM.

MEAT EXTRACTS. *Historical.* It is well known that extract of meat consists of beef tea evaporated to the consistency of a thick syrup. It therefore contains the whole of those constituents of meat which are soluble in hot water.

It was first correctly prepared in 1821 by Proust, by whom, in conjunction with Parmentier, it was very highly recommended as a stimulant quite as valuable for the strong and healthy as for invalids. In 1847 Liebig, in his celebrated treatise on 'Researches on the Chemistry of Food,' most warmly approved of Proust and Parmentier's extract, and subsequently made every effort to popularise the use of the preparation. The attention of many men of science, but more particularly of the medical profession in Germany, was attracted to Liebig's abstract scientific researches into the nature of meat, and it was ascertained that extract of meat was of great usefulness in medical cases.

In consequence, the *Extractum Carnis* was, without Liebig's assistance, introduced into the Bavarian Pharmacopœia of 1856, and from that time all Bavarian apothecaries were legally bound to keep the extract in stock, or to make it when required, just as any other drug. From Bavaria the knowledge and medical use of the extract spread over the whole of Germany, but its manufacture remained confined to pharmaceutical chemists, and its use to the sick-chamber. Liebig, on the other hand, while fully appreciating the clinical importance of the extract, and further endeavouring to improve the alimentation of sick persons by various modifications of this invention, proposed to bring meat extract into commerce as an article of food, and to make its manufacture the object of industrial enterprise on a large scale. His endeavours were, however, without success until, early in 1862, George Christian Giebert, an engineer, well acquainted with the meat-producing districts of South America, went to Munich to receive instruction in the method of preparing the extract by Liebig himself, aided by von Pettenkofer, and then returned to Uruguay and established a manufactory on a considerable scale. In November, 1864, the first samples of Giebert's manufacture arrived at Munich and their quality far exceeded the expectation of Liebig. He consented to Giebert's proposition that the extract should bear the name of the inventor, on condition that it should always be free from fat and gelatin, and that each consignment should be subjected to a gratuitous analysis by him or his delegate.

The industry has flourished and immense areas of land are farmed to produce cattle required for the manufacture of meat extracts. Take, for example, some facts connected with the enterprising company to which Liebig gave permission to bear his name. The Liebig's Extract of Meat Company farmed, in 1868, some 28,494 acres of land, and the total herd of horned cattle reared on this area was 12,000. In 1908, the acreage was 1,302,386 and the number of cattle 224,406, and in 1922 the acreage was 5,250,000, of which 2,500,000 acres are in South Africa—the total head of cattle carried on these areas being approximately 500,000. Striking as the figures may be as illustrating the enormous expansion of the cattle-rearing industry, they become still more impressive when regard is paid to the fact that the cattle are no longer, as in Liebig's day, and according to his own words, 'half-wild animals,' but are bred from the choicest pedigree stock taken from the farms of our best English breeders.

Each animal is allotted about 5 acres of pasturage. The average daily amount of grass consumed by one animal is 88 pounds; a herd of 250,000 would therefore consume *per diem* 22,000,000 pounds of grass, or approximately 10,000 tons. Thus the yearly consumption of grass would mean not far short of 4,000,000 tons The composition of pasture grass, according to the average of a large number of analyses, is as follows:—

	Per cent.
Water	80·00
Proteins with a small quantity of nitrogenous extractives[1]	3·50
Fat	0·80
Carbohydrates	9·70
Fibre	4·00
Mineral salts	2·00
	100·00

This means for a herd of 250,000 head [illegible] cattle per year a food yield in the form of grass of the following quantities of its individual solid constituents:—

	Tons
Protein or flesh-forming substances	140,000
Fat	32,000
Carbohydrates	388,000
Fibre	160,000
Mineral salts	80,000
	800,000
Balance due to 80 p.c. of water in grass	3,200,000
Total	4,000,000

Similarly, the annual amount of water consumed, based on the fact of one animal requiring 30 litres per day, would amount to 700,000,000 gallons per annum for the herd. These figures refer only to the stock of one company. The Argentine, Uruguay, and Paraguay republics are immense fodder-yielding tracts, and the metamorphosis of grass proceeds steadily and uninterruptedly day by day on a colossal scale. There are occasions when the ordinary grass is supplemented by 'Alfalfa,' a rich clover corresponding to our lucerne and containing a good proportion of nitrogenous food.

Method of manufacture. In principle the lines laid down by Liebig, which he considered essential to success, are still followed by the Liebig Company. In the first place, the meat is hung in the cooling halls for 12 or more hours, then the fat and sinews are carefully removed, and the meat is fed to chopping machines with revolving knives From the chopping machines the meat emerges in chunks, which drop into mincing machines especially constructed for the purpose. The meat emerges from these machines as mincemeat, and is then transferred to the extracting pans, each capable of holding about 4 tons, in which it is left with its own weight of pure filtered water. After the addition of more water the mixture is heated to a temperature not exceeding 95° by means of steam jackets. During this time fat continuously rises and is skimmed off. The more or less clear liquor is then run off and the work of concentration is commenced. Fat is again skimmed off until at length the extract or soup is practically fat-free. Concentration proceeds again *in vacuô*, and during evaporation is twice filtered before passing into the final concentrator, which is fitted with a revolving worm through which low pressure steam is passing. Constant stirring during the final stages of evaporation is essential to secure uniformity in regard to consistency and composition of the finished extract. The treacly mass is then run off while hot into 100 lb. tins, cooled, hermetically sealed and dispatched to the European blending factories.

The extract is finished within 3 days of the death of the animal.

One thousand pounds of lean meat, treated upon a manufacturing scale, furnishes 31 lbs. of extract. A standard extract manufactured as described contains an average of 18·25 p.c. moisture, 61·5 p.c. of organic matter, 20·25 p.c. of mineral substances, and yields an alcoholic extract of 57 p.c.

It should be as free as possible from gelatine, fat, and coagulable or insoluble albumen. By far the greater proportion of the meat constituents, namely, the fibrine, gelatine-yielding tissue, and fat is therefore rejected in the preparation of extract.

Lemco, a typical first grade extract, has the following composition:—

		Per cent.
Water		20·05
Organic matter		58·52
Mineral matter		21·43
		100·00
The mineral matter contains:		
Combined chlorine		1·88
Phosphates as P_2O_5		6·00
The organic matter contains:		
Total nitrogen		9·45
Distribution of the total nitrogen:		
Nitrogen in fibrine and albumen	0·14	
,, meat bases soluble in alcohol	5·64	
,, meat bases rendered insoluble in alcohol	0·70	
,, gelatine	0·02	
,, albumoses	1·73	
,, peptones	1·17	
Ammoniacal nitrogen	0·05	
	9·45	
Creatine		1·85
Creatinine		4·95
Total		6·80
Fat (ether extract)		0·12

The meat bases constituting the essential part of the extract contain creatine, creatinine, xanthine bases, carnine, carnic acid, and other complex organic bodies.

Reference may be made here to the ratio between the creatine and creatinine in the above analysis which is as 1 : 2·6. The creatine of the meat has been altered to the anhydride creatinine by loss of water during evaporation. Experience has shown this to be reversed on storage, water being taken up and creatine again formed

Whilst all commercial extracts are essentially of the same character, the proportions and derivation of the various constituents differ. The following analyses in Table I. may be taken as representing the composition of the leading meat extracts on the British market:—

---

[1] N × 6·25.

TABLE I.

	Average composition of			
	Oxo p.c.	Bovril p.c.	Hospital Oxo p.c.	Bovril for Invalids (enriched) p.c.
Water . . .	40·42	44·09	28·35	29·63
Organic matter .	40·42	38·65	55·12	54·36
Mineral matter .	19·16	17·26	16·53	16·01
	100·00	100·00	100·00	100·00
The mineral matter contains:				
Combined chlorine	6·70	6·07	5·06	4·23
Phosphates as P_2O_5	2·69	2·48	2·41	3·21
The organic matter contains:				
Total nitrogen .	5·95	5·82	8·37	8·47
Distribution of the total nitrogen:				
Nitrogen in fibrine and albumen .	0·88	1·06	1·51	1·89
Nitrogen in meat bases soluble in alcohol . .	2·41	2·36	2·25	2·66
Nitrogen in meat bases rendered insoluble in alcohol	0·50	0·66	0·70	0·77
Nitrogen in gelatine and hydrolised gelatine . .	1·24	1·03	2·87	2·52
Nitrogen in albumoses . .	0·21	0·20	0·0	0·14
Nitrogen in peptones . .	0·67	0·49	0·98	0·42
	5·91	5·80	8·31	8·40
Creatine . .	1·65	1·65	1·76	1·75
Creatinine . .	1·61	1·44	1·37	1·52
Total . .	3·26	3·09	3·13	3·27

A practice has arisen of mixing meat extracts with extracts of yeast. The extract of yeast has valuable dietetic properties and contains the active principles of fermentation. It also resembles, in many respects, physically and chemically, but not in taste, extract of meat. The addition of more than 2 p.c. of this to a meat extract imparts a distinctive taste.

According to Wiley the presence of yeast extract in meat extract can be determined by treating the mixture with a strong solution of zinc sulphate and filtering. In meat extract the filtrate obtained is always quite clear, but when a yeast extract is present the filtrate is turbid. Hehner applied the Folin reaction for the estimation of creatine and creatinine in meat extracts, and as yeast extract contains neither creatine nor creatinine, the test is of importance in determining the source and value of a meat extract.

The Folin method for the estimation of creatinine is a colorimetric one, based on the fact that creatinine gives with picric acid, in presence of alkalis, an orange to deep red solution, the intensity of the coloration depending upon the amount of creatinine present (Zeitsch. physiol. Chem. 1904, 41, 223). Folin recommends the use of Dubosq's colorimeter for making the colour comparisons.

The test is carried out as follows: With good quality extracts 5 grams are dissolved in water and the solution made up to 500 c.c.

Creatinine. 20 c.c. of this solution are taken for the determination of creatinine, viz. 0·200 gram of extract. To 20 c.c. of the solution in a 500 c.c. flask are added 20 c.c. of picric acid solution (saturated) and 5 c.c. of a 10 p.c. caustic soda solution.

The mixture is shaken and allowed to stand exactly 5 minutes, and is then made up to 500 c.c. with pure water at 18°, and its colour compared with that obtained from a standard solution of potassium dichromate (24·565 grams per litre).

All colorimetric readings are made with a Dubosq colorimeter, having the left-hand cylinder fixed at exactly 8 mm. depth of bichrome solution.

The following readings were obtained:—

8·2 mm. 8·1 mm.
8·2 ,, 8·0 ,, Jaffe's formula
8·1 ,, 8·0 ,, 8·11)81·00(9·99 mgms.
8·1 ,, 8·1 ,, creatinine.
8·2 ,, 8·1 ,, 9·99 mgms. found in
— — 0·2 grm.
8·16 ,, 8·06 ,,
Average 8·11 mm.
0·2 : 100 : : 0·0099 : x
x = 4·99 p.c. creatinine.

Total creatinine and creatine. 15 c.c. of the extract solution (5 grams in 500 c.c. water) = 0·15 gram extract, are placed in a porcelain basin 8 cm. diameter, and 10 c.c. of normal HCl (1 c.c. = 0·0365 gram HCl) added, and slowly evaporated to dryness on a water-bath taking at least 2 hours for the evaporation. The residue is dissolved in 15 c.c. of water, then to the contents in the basin 20 c.c. picric acid are added, and 5 c.c. of the caustic soda solution. The mixture is stirred with a glass rod, and exactly after 5 minutes' standing transferred to a 500 c.c. flask, the basin being washed out several times into the flask, and the liquid made up to 500 c.c. at 18°. The following readings were obtained:—

8·4 mm. 8·5 mm.
8·4 ,, 8·6 ,, Jaffe's formula
8·5 ,, 8·6 ,, 8·49)81·00(9·54 mgms.
8·4 ,, 8·6 ,, creatinine.
8·4 ,, 8·5 ,, 9·54 mgms. found in
0·15 grm. extract.
8·42 ,, 8·56 ,,
Average 8·49 ,,
As 0·15 : 100 : : 0·00954 : x.
x = 6·36 p.c.

6·36 p.c. acid treated.
4·99 p.c. creatinine.
—
1·37 creatinine due to creatine.
1·16 factor for converting creatinine to creatine.

$$1·37 \times 1·16 = 1·5892 \text{ creatine.}$$

Corrected results:

Creatinine	4·99 p.c.
Creatine	1·59 ,,
	6·58 ,,

In carrying out this test care must be taken to observe all the details as regards:

(*a*) Strength of solutions employed;

(*b*) Time of contact;

(*c*) Dilution of original liquid;

(*d*) Depth in mm. of the unknown solution should be within the range of 7 mm. and 9 mm.;

(*e*) Temperature to be as near 18°C. as possible

With extracts that yield low creatine and creatinine figures it is necessary to treat the extract before applying the test. 10–50 grams of the substance are dissolved in the smallest bulk of water possible. Then 250 c.c. methylated spirits are added and allowed to stand for 12–16 hours, filtered, the alcohol distilled off, the residue dissolved in water, and made up to 100 c.c., an aliquot part not exceeding 20 c.c. being taken for the estimation.

It has been pointed out by Jaffé (Zeitsch. physiol. Chem. 1886, 10, 391), and more recently by A. C. Chapman (The Analyst, Nov. 1909), that other substances, such as acetone, dextrose, and lævulose reduce picric acid and produce the same coloration. When the presence of any reducing substance other than creatinine is suspected, preliminary treatment with methylated spirits is desirable. *See* further, CREATINE and CREATININE, Vol. II. pp. 410 and 412.

Methods of analysis. For the examination of commercial high-grade extracts the following method is applied.

In some meat extracts during the cooling in pots, crystals and other solids settle to the bottom before the mass becomes semi-solid, consequently the material must be well mixed without warming before analysis.

Water. 2 grams are evenly spread by means of a glass rod round the inside of a porcelain crucible 37 mm. high and 55 mm. wide on top to within 10 mm. of top edge; dried for 36 hours in a water-oven at a temperature of 97°, cooled for 20 minutes in a desiccator over vitriol and quickly weighed. A Moslinger's cellular water-oven is best for this class of work.

Ash. 2 grams are weighed in a platinum basin and slowly burned without the basin becoming visibly red. The burner employed has a round cover 7 cm. in diameter with 28 holes, each 1 mm. in diameter. After carbonising, the mass is crushed twice and the ash obtained should be a greyish-white without showing fusion—too strong or too quick ignition will cause loss.

For absolutely correct ash estimation the basin is put on an asbestos sheet to protect the contents from sulphurous acid of the gas, or better still, burned in an electric furnace at 6–8 ampères until the ash is clear grey. This is weighed when cold and washed into a small beaker, acidified with nitric acid, and warmed until the light brown coloured matter coagulates. Filter and use the filtrate for the chlorine estimation, wash the carbonaceous matter from the filter into a small crucible, dry at 105° and weigh. Deduct this carbon from the former weight to get the true pure ash.

The chlorine is estimated in the acidified filtrate from the ash gravimetrically, as phosphates interfere with the volumetric estimation.

Alcoholic extract. By this is meant that portion of the extract soluble in ethyl alcohol, 80 p.c. by volume. 2 grams are weighed out into a small Soxhlet flask, 9 c.c. water added, and the extract dissolved without warming, 50 c.c. alcohol (93 p.c. by volume, sp.gr.=0·8234) slowly added with gentle shaking, allowed to stand over night at 17°–18°, and then carefully poured from the fast-sticking mass into a weighed porcelain basin 76 mm. diameter and 34 mm. deep; the alcohol is evaporated slowly on a water-bath at 70°–75°. In order to prevent creeping the basin is placed on a layer of flannel over the hole in the bath, or in a copper basin soldered into the opening in the bath and having a layer of sand between the copper and porcelain basins. Meanwhile to the insoluble mass in the flask 50 c.c. alcohol of sp.gr. 0·8639 (80 p.c. by volume) are added with gentle shaking and allowed to stand at 17° until the first alcoholic solution is evaporated when the second portion is decanted into the basin, and this again evaporated until the contents have the consistency of honey. The basin is then dried at 98° in the water-oven for exactly 6 hours, cooled 20 minutes in the desiccator, and quickly weighed. The extraction temperature must be within 17°–18°, or variable results will be obtained.

GENERAL ANALYSIS OF MEAT EXTRACTS.

Modified Stutzer method. 30 grams are weighed, dissolved in water and made up to 250 c.c. A fair average sample is thus obtained, and all estimations necessary can be begun the same day.

Moisture. Cleaned ignited Calais sand is put into a flat nickel basin 9 cm. in diameter along with a small glass stirring rod until the whole weighs exactly 100 grams. Dried in steam oven until weight is constant, then 25 c.c. extract solution added (=3 grams extract), stirred amongst the sand, evaporated until granular on a water-bath, transferred to a steam oven for 36 hours, cooled and weighed.

Ash. 25 c.c. (=3 grams) evaporated and carbonised. Owing to the quantity of carbonaceous matter the estimation of ash cannot well be made direct, hence the charred mass has to be extracted three times with boiling water, and filtered through an ashless filter paper into a porcelain basin, the char and filter paper burned off in the platinum basin, and the filtrate put back in the platinum basin, evaporated, dried, ignited gently, and weighed. The ash is dissolved in cold water, acidified with nitric acid, made up to 250 c.c., and used for estimation of chlorides and phosphates.

Chlorides are estimated gravimetrically in 50 c.c.

Phosphates are estimated by the molybdate and magnesia mixture method in 50 c.c.

Fibrine and **already coagulated albumen.** 25 c.c.(=3 grams) are diluted and settled in a 100 c.c. cylinder over night. The top liquid decanted and the residue either transferred to a counterpoised filter, washed, dried at 100°, and weighed, or the residue transferred to a centrifuge tube, washed, and the nitrogen estimated by Kjeldahl's method.

Soluble albumen. The decantations from the above are acidified with acetic acid, boiled for

5 minutes, settled, filtered, and weighed or treated by Kjeldahl's process. If the total fibrine and albumen together be required, then it is only necessary to acidify 25 c.c. of extract solution diluted to 100 c.c., with acetic acid, boil for 5 minutes, settle, filter, and either weigh at 100° or estimate by Kjeldahl's method.

Gelatine. 25 c.c. of extract solution (=3 grams) are poured on to asbestos fibre in a small porcelain basin, evaporated to dryness, extracted with 93 p.c. alcohol three times, then with ice-cold water containing 10 p.c. alcohol, until the decantations are free from colour (the temperature must never rise above 5°). The gelatin is either dissolved and washed from the asbestos and treated by Kjeldahl's process, or the asbestos and gelatine may be put direct into the Kjeldahl flask. With some extracts it is better to take 25 c.c. extract solution, and, without evaporating, add 250 c.c. methylated spirit, stand 8 hours, decant off alcohol from the sticky mass and wash with 10 p.c. ice-cold alcohol until free from colour, then treat by the Kjeldahl method.

Total nitrogen. 10 c.c (=1·2 gram extract) are treated by Kjeldahl's method direct

Meat bases soluble in alcohol. 25 c.c. (=3 grams extract) taken in beaker, 250 c.c. absolute alcohol added with constant stirring and settled for 12–16 hours. The alcohol passed through filter into a 500 c.c. round-bottomed flask, the residue washed twice with 25 c.c. absolute alcohol, and the alcohol distilled off, standing the flask inside a water-bath. The meat bases are then treated by the Kjeldahl process in the flask without transference so as to avoid loss.

Residue insoluble in alcohol. The insoluble residue from the absolute alcohol is dissolved in water on the water-bath. A few drops of acetic acid added to coagulate the soluble albumenoids, then boiled and filtered into a 250 c.c. flask for the estimation of gelatine, albumoses, and peptones. The residue on the filter, consisting of fibrine and albumen, may be treated by Kjeldahl's method as a check on former estimation.

Total nitrogen in gelatine albumoses and peptone fraction. 50 c.c. of the 250 c.c. taken for the Kjeldahl process.

Albumoses and gelatine. 50 c.c. of the 250 c.c. are taken in a porcelain basin, and powdered zinc sulphate crystals added with frequent stirring until saturated and allowed to stand overnight. The precipitate is filtered, washed with saturated zinc sulphate solution, and subjected to Kjeldahl's process. The filtration of the precipitate is slow, but proceeds steadily, and works better if the liquid is rendered slightly acid with sulphuric acid (1 : 4).

Peptones, albumoses, and gelatine. 50 c.c. of the 250 c.c. are put into a beaker 50 c.c. sulphuric acid (1 : 3) added, and an excess of phosphotungstic acid, prepared by making a strong solution of sodium tungstate in boiling water, and adding phosphoric acid with continued boiling until the mixture gives a constant acid reaction.

An alumina-like precipitate is formed which, if left for a few hours, filters fairly well. The precipitate is washed several times with dilute sulphuric acid, and then treated by Kjeldahl's method. This operation has to be carefully conducted as the precipitate causes bumping.

The nitrogen from this estimation comes almost up to the total nitrogen of the section insoluble in alcohol, but a little of the meat bases are sometimes rendered insoluble by the alcohol, and the traces obtained by difference are to be added to the meat bases. Having obtained the gelatine figure by a separate estimation, then (gelatine and albumoses) − gelatine = albumoses, and (gelatine + albumoses + peptones) − (gelatine + albumoses) = peptones.

Ammoniacal nitrogen. Traces only of this are present, 50 c.c. of the standard extract solution (=6 grams extract) are distilled with barium carbonate into standard acid.

All nitrogen determinations are made by the Kjeldahl-Gunning method, using about 25 c.c. nitrogen-free vitriol to start with. After frothing, and the thick carbonaceous mass has disappeared, 40 grams of potassium sulphate and a small crystal of copper sulphate are added. Heating must be continued until the yellow colour has changed to a clear blue, indicating complete oxidation. In distilling off the ammonia it is preferable to use steam with a small flame under the alkaline liquid to prevent dilution by condensation, instead of a naked flame under the distillation flask. Zinc-dust is added to separate the copper, and to prevent bumping. The period of distillation should be 40 minutes

In calculating the percentage of the various nitrogenous compounds in extracts it is usual to use the factor N × 6·25. This is not, however, strictly accurate, but is generally accepted as the best approximation to the truth. Analyses, therefore, should disclose the actual nitrogen figures obtained. The use of nitrogen factors is discussed in Analyst, 1915, 40, 310–326.

An auxiliary method for the estimation of gelatine and hydrolised gelatine is that of Beckmann (Forschungs Berichte, 1896, 3, 324) based upon the fact that gelatine and albumenoids are rendered insoluble by formaldehyde. 3 grams extract dissolved in 20 c.c. cold water are treated with 3 or 4 drops of formaldehyde solution (40 p.c. strength) and evaporated to dryness on a water-bath and for 2 hours in an air oven, then moistened with a 5 p.c. formaldehyde solution, and after standing 5 minutes, warm water, 60°–70°, is added and allowed to digest 15 minutes, the water is then decanted, and the washing repeated until free from colour. The insoluble mass is subjected to the Kjeldahl process. Care must be observed to use a formaldehyde solution which is neutral, since free acid affects the reaction.

A convenient method for the determination of the total soluble proteids in extract is based on the fact that halogens precipitate those bodies. Bromine water is for convenience employed. Allen and Searle take 1 gram of the substance dissolved in 100 c.c. water in a flask and acidify with dilute hydrochloric acid. A considerable excess of bromine water is added and the liquid shaken for some time. The precipitate is allowed to settle for several hours, the supernatant liquid decanted through an asbestos filter, the precipitate washed with cold water and treated by Kjeldahl's method. Van Slyke's method of protein analysis (Vol. IV. 403, and Plimmer's Biochemistry, 1915, 146–149) has been applied by Hartley to the determination of the amino nitrogen contents of meat extract. He found that of the total nitrogen 12 p.c. was in the amino form, being liberated on treatment with nitrous acid. The method can be carried out in fifteen minutes, and enables the analyst to at once differentiate the various forms of nitrogen in this and similar substances (*see* Analyst, 1915, 40, No 472, 310–326; *cf.* Smorodinzer, Zeitsch. physiol. Chem. 1914, 92, 214). On the changes in the composition of the nitrogenous constituents of meat extracts, *see* Wright, J. Soc. Chem. Ind. 1911, 30, 1197; *ibid.* 1912, 31, 176. F. S.

MECCA BALSAM. *Opobalsam*; *Balm of Gilead* (*v.* Oleo-resins).

MECONIC ACID, MECONIDINE *v.* Opium.

MECONINE *v.* Lactones.

MEDINAL. A sodium compound of veronal. Used as a hypnotic.

MEDLAR. The fruit of *Mespilus germanica* (Linn.). When fresh, the fruit has a yellowish-white flesh, which is hard and of an unpleasant astringent taste; on keeping for some weeks, the flesh becomes brown, soft, and doughy, and possesses an agreeable flavour. In the latter condition, Bersch (Landw. Versuchs. Stat. 1896, 46, 471) examined the various parts of the fruit and obtained the following results:—

Percentage	Whole fruit	Rind	Flesh	Pips
of dry matter	30·9	36·9	24·8	61·6

The dry matter contained—

	Protein	Fat	Invert sugar	Other N-free extract	Crude fibre	Ash
Whole fruit	2·79	1·04	36·08	40·98	16·29	2·82
Rind .	4·12	2·66	—	72·62	17·51	3·09
Flesh .	2·62	0·57	48·56	37·63	7·35	3·27
Pips . .	2·55	0·62	—	46·66	48·52	1·65

Malic acid, acetic acid (0·03 p.c.) and alcohol were present.

The ash of the medlar has been found to contain about 0·3 p.c. boron trioxide. In the N-free extract there is a considerable portion of pectin matter. H. I.

MEDULLADEN *v.* Synthetic drugs.

MEDULLIC ACID $C_{20}H_{41}{\cdot}CO_2H$, m.p. 72·5°, an acid found as a glyceride in beef suet and in beef marrow, associated with oleic and palmitic acids.

MEERSCHAUM or **SEPIOLITE.** A hydrated magnesium silicate $H_4Mg_2Si_3O_{10}$, occurring as nodules and compact masses, of white, grey, or creamy colour. From its appearance and its extreme lightness (sp.gr. about 2) it has acquired the name of *meerschaum* or 'sea-froth' (*écume de mer*), although it is sometimes described by mineralogists under the name of *sepiolite*, a word introduced by Glocker to indicate its resemblance to the light white porous material known as the bone of the cuttle-fish or sepia. Meerschaum is a soft mineral (hardness 2–2·5), easily carved; has a greasy feel, and readily adheres to the tongue. In consequence of its porosity, a meerschaum pipe absorbs the oily matter of the tobacco; and for a like reason the proportion of water present in the mineral depends on the humidity of the atmosphere. In a moist atmosphere the composition corresponds with $2MgO{\cdot}3SiO_2{\cdot}4H_2O$, with 21·7 p.c. water. About half of this water is lost over sulphuric acid, and the remainder is expelled only at a high temperature, about 300°. Up to this temperature the mineral retains its optical characters, the formula being then $2MgO{\cdot}3SiO_2{\cdot}2H_2O$ (with 12·2 p.c. water). The following analyses illustrate the composition of meerschaum:—

	I	II	III
Silica . .	60·87	61·30	53·8
Magnesia . .	27·80	28·39	23·8
Alumina . .	—	—	1·2
Water . .	11·29	9·74	20·0
	99·96	99·43	98·8

I. From Asia Minor, by Lynchnell. II. From Greece, by Scheerer. III. From near Madrid, by Berthier.

Meerschaum is found as nodular masses in alluvial deposits in the plains of Eski-Shehr, in Asia Minor, where it is associated with compact magnesite ($MgCO_3$) and serpentine. It is here dug from a number (now some 1270) of shallow pits, from the bottom of which short galleries are occasionally run. The nodules are scraped free from earthy matter with a special knife, air dried, polished with wax, and sorted into a number of grades and sizes (J. Soc. Arts, 1909, 57, 411). It also occurs at Kiltschik, near Konieh, in Natolia; in Greece, Negroponte, and Samos; in Moravia; with magnesite and serpentine at Kraubat in Styria; and in New Mexico. In New Mexico it occurs as nodules and seams in limestone, and has been exploited at two localities, namely Gila valley and Bear Creek in Grant County (D. B. Sterrett, Bull. U.S. Geol Survey, 1908, No. 340, 466). At Vallecas, near Madrid, it is said to be used as a light material for constructive purposes. Meerschaum has been employed as an ingredient in porcelain, while in Turkey it is used, when fresh, in the place of soap, and as a kind of fuller's earth. From the East large quantities are sent to Vienna to be carved as tobacco pipes. The pipes are prepared for use by being soaked in melted tallow and wax, and are polished with shave grass. Imitations are fabricated in plaster of Paris hardened with paraffin, and in a preparation of potatoes treated with dilute sulphuric acid. L. J. S.

MEGASSE. Spent or crushed sugar-cane.

MEILER. The German name for the stack of timber piled up for burning into charcoal (*v.* Carbon).

MEKOCYANIN *v.* Anthocyanins.

MELACONITE or **BLACK COPPER.** Cupric oxide, CuO, crystallised in the monoclinic (or perhaps triclinic) system. As a black, sooty powder, soiling the fingers, it is of frequent occurrence on the weathered surface of copper-pyrites and other ores of copper. In the massive form it is sometimes found in considerable quantity, sufficient for use as an ore of copper, *e.g.* in the Ducktown mines in Tennessee, Copper Harbor, or Lake Superior in Michigan, Bisbee in Arizona, and Copiapo in Chili. Crystals are rare and have the form of minute scales with a steel-grey colour and brilliant metallic lustre; sp.gr. 5·82. They have been found only in Cornwall and on lava at Vesuvius. The name *tenorite* was applied to the Vesuvian crystals; and the name melaconite (from μέλας, black, and κόνις, dust) is more properly used for the earthy, probably colloidal, form, which contains admixtures of hydrated silicate and carbonate of copper and grades into melanochalcite (G. A. Koenig, 1902) and pitchy copper-ore. L. J. S.

MELANTERITE or **IRON VITRIOL.** Hydrated ferrous sulphate, $FeSO_4{\cdot}7H_2O$ crystallised in the monoclinic system. As a mineral, this is usually found as a white, silky, fibrous efflorescence, resulting from the decomposition by weathering of iron-pyrites and marcasite. Stalactitic and concretionary masses also occur, but well-formed, green crystals similar to those obtained artificially are rare. It is of wide distribution, but usually only in small amounts. Considerable quantities were, however, formerly obtained from the pyrites mine at Goslar in the Harz. L. J. S.

MELDOLA'S BLUE *v* OXAZINE COLOURING MATTERS.

MELDOMETER. An instrument designed for the purpose of ascertaining the melting and boiling points of small quantities of substances It consists essentially of two pairs of forceps mounted on a stage and carrying between them a thin platinum ribbon. Through this ribbon an electric current may be passed, the strength of the current being regulated by a carbon-mercury rheostat. The apparatus is mounted on the stage of a compound microscope, provided with a 1-inch objective. The substance to be examined is placed in focus on the platinum ribbon, and then the current is gradually increased until the substance is melted or volatilised. Experiments made in this way show interesting phenomena, sufficiently characteristic in many cases to identify a substance at once. By arranging side by side different fragments it is easy to find their order of melting-points with greater exactness than can be the case when the blow-pipe is employed.

The meldometer is also of value in studying sublimates. A piece of glass is held over the heated strip and upon this the sublimate deposits. A long series of trials have led to the conclusion that the appearances so obtained are excellent as tests to the mineralogist and chemist (J. Joly, Industries, 1889, 29, and J. Soc Chem. Ind. 8, 306).

MELEZITOSE *v.* CARBOHYDRATES.

MELIBIOSE *v.* CARBOHYDRATES.

MELICITOSE *v.* CARBOHYDRATES.

MELILITE. A rock-forming mineral consisting of silicate of calcium, aluminium, iron, magnesium, and sodium, crystallised in the tetragonal system. The formula is uncertain, and, like the allied minerals gehlenite, åkermanite (known only as an artificial product in slags), and fuggerite, its composition may be explained by isomorphous mixtures of the following molecules: $3CaO{\cdot}Al_2O_3{\cdot}3SiO_2$ (sarcolite), $3Na_2O{\cdot}Al_2O_3{\cdot}3SiO_2$ (a hypothetical soda-sarcolite), $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$ (velardeñite), and åkermanite ($4MgO{\cdot}8CaO{\cdot}9SiO_2$). Melilite forms short square prisms resembling cubes; its colour is white, grey, yellow (hence the name, from μέλι, honey) or brown. Sp.gr. 2·9–3·1, H. 5. It occurs principally in volcanic rocks poor in silica and rich in alkalis, *e.g.* in melilite-basalt and in the leucite lavas near Rome. It is also found in the blocks of metamorphosed limestone enclosed in the vesuvian lava on Monte Somma. It is frequently found as well-developed crystals in the slags of blast furnaces, and has been observed in Portland cement clinkers. L. J. S.

MELINITE *v.* EXPLOSIVES.

MELISSA. The leaves and tops of *Melissa officinalis* (Linn.) contain a small quantity of a volatile oil. They are used occasionally in the form of a warm infusion as a diaphoretic in slight febrile conditions.

MELISSIC ACID $C_{29}H_{59}COOH$ is obtained by heating melissyl alcohol with soda-lime at 220° until hydrogen ceases to be evolved (Stürcke, Annalen, 223, 295); m.p. 91° (Marie, Ann. Chim. Phys. [vii.] 7, 145); 90° (Heiduschka and Gareis, J. pr. Chem. 1919, [ii.] 99, 293. It is probably identical with an acid found in beeswax (Nafzger, Annalen, 224, 225; Marie, *l.c.*); according to Heiduschka and Gareis, the acid from beeswax has the composition $C_{31}H_{62}O_2$ and melts at 88·5°.

MELISSIN, MELISSYL ALCOHOL *v.* WAXES.

MELITOSE, *Raffinose* (*v.* CARBOHYDRATES).

MELLITIC ACID. *Benzenehexacarboxylic acid* (Ger. *Mellithsaure*) $C_6(CO_2H)_6$. Obtained by oxidising charcoal with fuming nitric acid, fuming nitric acid and potassium perchlorate, or with sulphuric acid (Dickson and Easterfield, Chem. Soc. Proc. 1898, 163; Staudenheimer, Ber. 1899, 2824; Hübner, Chem. Zeit. 1890, 440; Verneuil, Compt. rend. 1907, 132, 1340; Bartoli and Papasogli, Gazz. chim. ital. 15, 546; Schulze, Ber. 1871, 802, 806; Meyer and Steiner, Monatsh. 1914, 35, 475; also *v. infra*). By the electrolysis of alkaline solutions, using graphite electrodes, mellitic acid $C_6(CO_2H)_6$, hydromellitic acid $C_6H_6(CO_2H)_6$, and pyromellitic acid

$$C_6H_2(CO_2H)_4$$

are formed (Bartoli and Papasogli, Gazz. chim. ital. 1882, 113; 1883, 37). Also formed together with pyromellitic acid as a decomposition product of sugar (Lippmann, Ber. 1894, 3408; *ibid.* 1917, 50, 236). Has been synthesised by passing a current of methyl chloride through a warm solution of toluene containing aluminium chloride and oxidising the hexamethylbenzene thus formed with potassium permanganate (Friedel and Crafts, Compt. rend. 91, 257; Ann. Chim. Phys. [vi.] 1, 470). Mellitic acid is best prepared in the following way: Carbon, fine enough to pass through an 80 or 90 sieve is boiled vigorously with nitric acid (sp.gr. 1·5) until the liquid becomes faintly amber in colour; this usually takes 3 days. The excess of nitric acid is distilled off at 130°–140° and the residue, containing 80–90 p.c. mellitic acid extracted with water (Holliday & Sons and Siberrad, J. Soc. Chem. Ind. 1908, 522; Eng. Pat. 24662; D. R. P. 214252). According to Michael (Ber. 1895, 1631), the raw material may be purified by boiling with acetic acid, filtering and concentrating the filtrate.

For its preparation from diethyl mesitylene, *see* Philippi and Rie, Monatsh. Chem. 1921, 42, 5.

Mellitic acid decomposes when heated in an open tube at about 260° and has no definite melting-point under these conditions, but when heated in a closed tube melts at 286°–288° (Michael, Ber. 1895, 1631); crystallises in long needles, soluble in alcohol and ether: heat of formation, 546·8 cal.; heat of combustion, 788·2 cal. (Stohmann, Kleber, and Langbein, J. pr. Chem. [ii.] 40, 128); heat of solution +3·672 cal. at 20·4° (Berthelot, Compt. rend. 101, 685): dissociation of acid (Quartaroli, Gazz. chim. ital. 1905, 35, i. 470). It dissolves unchanged in boiling sulphuric acid, and is not acted on by chlorine, bromine, concentrated nitric or hydriodic acids. Dry distillation yields carbon dioxide and pyromellitic acid, and by strong heating with glycerol trimesic acid and carbon dioxide are produced. When mellitic acid is subjected to the action of dehydrating agents it is converted into the anhydride of pyromellitic acid. By boiling mellitic acid with benzoyl chloride *mellitic anhydride* $C_{12}O_9$ separates in colourless crystals, insoluble in cold water, but uniting with warm water to form mellitic acid. It gives characteristic colorations with various solvents, *e.g.* rose-red to bluish-red with naphthalene, retene phenanthrene, and fluorene, and bluish-green with nitrobenzene (Meyer and Steiner, Ber. 1913, 46, 813; Monatsh. 1914, 35, 475). By fusion with caustic soda, benzene and carbon dioxide are formed (Baeyer, Annalen, Suppl. 7, 5); reduction with sodium amalgam yields hydromellitic acid. By the electrolysis of the aqueous solution, the chief gaseous products are oxygen, hydrogen, and carbon dioxide, very little carbon monoxide being produced (Bouingué, Bull. Soc. chim. [ii.] 35, 561). Acetonitrile and mellitic acid give rise to the triimide, *paramide* $C_6(C_2O_2NH)_3$ and the diimide, *euchrone* $C_6(C_2O_2NH)_2(CO_2H)_2$, when heated at 225° 235° (Mathews, J. Amer. Chem. Soc. 20, 648). A warm aqueous solution of the acid acts on anhydrous or hydrated bismuth oxide producing bismuth mellitate $Bi_2C_{12}O_{12}$, which when heated under reduced pressure in closed tubes at 350° yields pyrophoric bismuth (Thibault, Bull. Soc. chim. 1904, [iii.] 31, 135). Mellitic acid condenses with resorcinol to form phthaleins (Silberrad, Chem. Soc. Trans. 1906, 1787; Green, Chem. Soc. Proc. 1907, 12) and with amino-phenols to form rhodamines (Silberrad and Roy, *ibid.* 1908, 204; J. Amer. Chem. Soc. 32, 189); these compounds are dyestuffs (Eng. Pat. 28638; J. Soc. Chem. Ind. 1903, 414). According to Van Loon (Ber. 1895, 1271), mellitic acid is not esterified by alcohol and acids; but Meyer (Monatsh. 1904, 25, 1201) states that by heating mellitic acid with methyl alcohol and sulphuric acid in a benzene bath, the *pentamethyl ester*, m.p. 141°–144°, is formed; at 100° a mixture of the pentamethyl and hexamethyl esters is produced and at higher temperatures the hexamethyl ester predominates. The *hexamethyl ester* melts at 187° and may be formed by the action of methyl iodide on the silver salt (Kraut, J. 1862, 281; Kraut and Busse, Annalen, 177, 273) or by the action of diazomethane on the acid (Pechmann, Ber. 1898, 501). The *hexaethyl ester* melts at 73°.

MELON. The fruit of various plants of the *Cucurbitaceæ* of tropical or sub-tropical countries. There are many varieties, among which may be mentioned musk melon, *Cucumis melo* (Linn.), and water melon, *Citrullus vulgaris* (Schrad.). The characteristic of melons is the large quantity of water which they contain, while the solid matter consists mainly of dextrose.

Bersch (Landw. Versuchs. Stat. 1896, 46, 473) found the following:—

	Sugar melon		Persican melon		Water melon	
	Whole fruit	Flesh	Whole fruit	Flesh	Whole fruit	Flesh
Water .	92·85	95·15	93·87	95·90	93·44	93·69
Dry matter	7·15	4·85	6·13	4·10	6·56	6·31

The dry matter contained—

		Protein	Fat	Dextrose	Other N-free extract	Crude fibre	Ash
Sugar melon	Whole	22 25	6·73	36 32	12·97	14·90	6·84
	Flesh	13 39	1·69	70·63	0·29	6·90	7·09
Persican melon	Whole	20·71	13·14	30·18	4·49	21·56	9·94
	Flesh	11 80	1·85	65·85	3·44	8·44	8·62
Water melon	Whole	13·74	6·89	37·36	21 74	15 41	4·86
	Flesh	9·73	1·06	66·73	16 95	1·95	3·58

The seeds of melons contain much oil (30–40 p.c.).

For analyses of the pulp of several varieties of melon, *v.* Sacc (Compt. rend. 94, 1126); also Jaffa (Rep. Agric. Expt. Stat. California, 1894–95, 155).

The ash of water melon is rich in potash and iron (Payne, J. Amer. Chem. Soc. 1896, 18, 1061). H. I.

MELONITE. Nickel telluride $NiTe_2$ crystallised in the hexagonal system. There is a perfect cleavage parallel to the base, and the mineral is usually found as foliated grains of a reddish-white colour with metallic lustre. It is found only in the Melones and Stanislaus mines in Calaveras Co., California, Boulder Co., in Colorado, and in New South Wales. L. J. S.

MELON PUMPKIN SEEDS. *Cucurbitæ semina* of the B.P. The ripe seeds of *Cucurbita maxima* (Duch.).

MELRUBIN. Trade name for sodium 1-phenyl-2·3-dimethylpyrazolone-4-amino methane suphonate.

MELTING-POINT. A knowledge of the melting-point of a substance, *i.e.* the temperature of its transition from the solid to the liquid state, is of importance for many reasons. Thus the melting-point of an *organic compound* affords a criterion of purity and constitutes a means of identification, and is of service in elucidating relations in chemical constitution.

Melting-points of *alloys* yield evidence of the existence of eutectics and compounds formed from the constituent metals.

Melting-points of *hydrates* may be used to determine their degree of hydration (Roozeboom, Zeitsch. physikal. Chem. 1893, 10, 477; Lidbury, *ibid.* 1902, 39, 453).

Melting-points of *silicates* serve to indicate the formation of double and complex silicates, and the dissociation of complex silicates into simpler molecules.

Melting-points of *pure substances* provide standards in calibrating thermometric apparatus.

Occasionally, on heating under ordinary conditions, sublimation occurs without melting, as in the cases of iodine and fumaric acid, when the usual methods are not applicable. But, generally speaking, every pure substance exhibits a definite melting-point, sharp and well-defined, and identical with its solidifying point The slightest impurities, however, such as traces of moisture, frequently lower the melting-point considerably, although it may be still apparently sharp; whilst if foreign substances are present in larger quantity, it is no longer well-defined, nor coincident with the solidifying point. It has been observed (Rohland, Chem. Zentr. 1906,

i. 1401) that in some instances addition of impurities may raise instead of lower the melting-point. Pure aluminium melts at a lower temperature than the impure metal, and alumina raises the melting-point of pure kaolin.

Within the ordinary limits, change of atmospheric pressure has no sensible effect upon the melting-point, but at high pressures the effects may be very considerable, *cf.* Demerliac (Compt. rend 1897, 124, 75); Hulett (Zeitsch. physikal. Chem. 1899, 28, 629); Tammann (Ann. Chim. Phys. 1899, [ii.] 68, 553, 629). The melting-point of benzene, for example, varies from 5·4° to 36·5° with pressures ranging from 1 to 1200 kilos. per sq. cm.

For theoretical relationships, *see* Thomson (Phil. Mag. [iii.] 37. 123), Negreanu (Chem. Zentr. 1906, i. 116).

Pawloff (Zeitsch. physikal. Chem. 1908, 65, 1; 1909, 65, 545) finds that even with a pure substance, the melting-point is affected by the state of subdivision, that is, it is dependent on the surface energy, and he deduces an equation expressing the relation between the melting-point of a substance and the radius of its granules. Experiments with salol showed that particles of less than 2μ diameter melt 1·1° lower than those of 40μ.

He considers that the lowest attainable temperature in the region of fusion is determined by the melting-point of the crystalline germ of maximum surface, and that larger solid particles above this temperature are super-heated. Similarly the super-cooling of liquids is a general phenomenon, a liquid super-cooled to a definite extent being in equilibrium with solid particles of a definite size, larger particles causing crystallisation and smaller particles dissolving, and the limit of super-cooling is that temperature below which the crystalline germ can arise of itself in the interior of the liquid.

Apart from the foregoing considerations, the manipulative details concerned in the actual determination of a melting-point, particularly by the capillary tube method, *v. infra*, affect the result. This is due partly to unequal heating of the thermometer stem, which may be corrected by adding the value $n(T-t)\times 0·000143$ to the observed point of fusion (n=length of mercury column in degrees outside the bath, T=observed temperature, and t = temperature registered in the middle of the projecting portion of the column), or avoided by using a short-stemmed thermometer (*see* Fig. 1). Irregular and too rapid heating is also found to affect the value. Schuyten (Chem. Zentr. 1901, ii. 1326) adduces instances of the variations which may be obtained under different conditions of experiment.

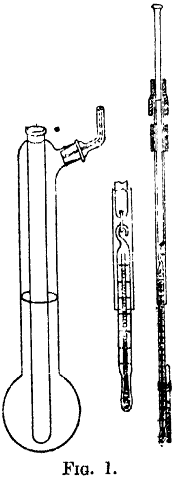


FIG. 1.

The fusion of a solid substance is accompanied by an absorption of heat ('latent heat of fusion'), the temperature remaining constant till all the solid has melted. This provides the most accurate means of determination (Landolt, Zeitsch. physikal. Chem. 1889, 4, 349), the thermometer, or thermo-element with galvanometer attachment, being immersed in the molten substance, and the temperature of the slowly cooling liquid noted at short intervals, the resulting curve indicating the stationary temperature. This method is suitable for all ranges of temperature and for all substances giving a definite melting-point, but requires the use of large quantities of material. In the case of organic compounds, a small quantity of the finely pulverised substance is introduced into a capillary tube closed at one end, and attached to a thermometer, close to the bulb, usually by a thin platinum wire or indiarubber ring, or by adhesion through a drop of sulphuric acid. Weyl (Chem. Zeit 1910, 34, 488) uses a thermometer slightly expanded just above the bulb, supporting a glass ring carrying glass hooks upon which the tubes are hung in position close to the bulb. Other methods of attachment are described by Lenz (Chem Zentr. 1906, i. 169); Landsiedl (Chem. Zeit. 1905, 29, 765).

The heating bath may be of glycerol, paraffin, or sulphuric acid, the last-named substance being most generally used. It is contained in a small beaker or long-necked flask, the thermometer and tube being either immersed in the liquid or enclosed in a tube dipping into the liquid.

A form of laboratory apparatus is shown in Fig. 2, unequal heating being avoided, as far as possible, by stirring with a glass stirrer passing through the cork holding the thermometer, or by heating very slowly with a small flame. For temperatures at which the escape of sulphuric acid fumes becomes unpleasant, the flask is provided with a side tubulure (Roth, Ber. 19, 1970), as shown in Fig. 1. Alternative apparatus for condensing the fumes are described by Houben (Chem. Zeit. 1900, 24, 538) and Matton (Zeitsch. angew Chem. 1910, 23, 557).

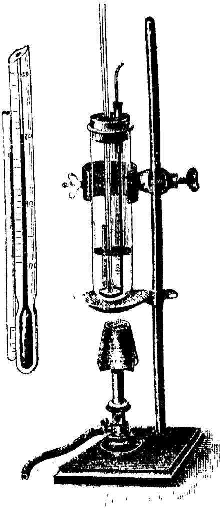


FIG. 2.

A mixture of three parts potassium sulphate with seven of sulphuric acid, sp.gr. 1 84, boiled together for five minutes, may be used for temperatures up to 325° From 360° to 600°, fused zinc chloride gives satisfactory results (Scudder, J. Amer. Chem. Soc. 1903, 25, 161).

Thiele (Ber. 1907, 40, 996) has devised a simple and effective apparatus, consisting of a glass tube 2 cm. diameter and 12 cm long, with a bent tube of 1 cm. diameter sealed in as shown in Fig. 3. Sufficient sulphuric acid is poured in to cover the upper opening of the bend, and the lower bend is heated by a small flame which causes an even circulation of the acid.

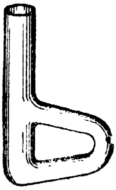


FIG. 3.

If the material is transparent, or becomes so before the melting-point is reached, observation of the exact point at which it liquefies is difficult, and Piccard (Ber. 8, 687) has proposed the apparatus shown in Fig. 4, in which the wide tube (*b*) is sealed after a small quantity of the substance has been melted and allowed to solidify in the capillary bend. On fusion the air pressure in *b* forces the liquid forward. The melting points of coloured substances are conveniently obtained in this way (Baither, Ber. 1887, 20, 3290). The values are, however, slightly too high.

As modified by Potilitzin (Chem. Zentr. 1893, i. 379) for the melting-points of salts, the apparatus consists of a glass tube, 5 mm. wide and 50 cm. long, drawn out to a capillary at one end, the other being bent first at right angles, and then in the shape of a **U** to form an open manometer. The capillary is sealed with the molten salt and immersed in the bath. When the salt melts, the mercury sinks in the open end of the manometer. The method is employed to advantage where a non-transparent heating bath is used.

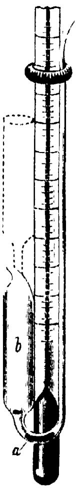


FIG. 4.

For organic compounds which decompose at or near the melting-point, Maquenne (Bull. Soc. chim. 1904, 31, 471) advocates the use of a metal block, rapidly heated, upon which the substance is thrown in small portions (0·1 m.g.) at a time, till the point is reached at which the substance melts instantaneously. *See also* Michael (Ber. 1895, 28, 1629).

Rassfeld (J. pr. Chem. 1916 [ii.] 92, 467) has devised an apparatus for determining melting-points above 270°, consisting essentially of an inverted **T**-tube, the horizontal limb of which passes through opposite sides of a small tin bath. The thermometer and capillary tube are adjusted in the vertical limb, so that the substance can be seen by looking through the horizontal tube against a light. An arrangement which is equally serviceable for high and low temperatures has been devised by Stock (Ber. 1917, 50, 156). It consists essentially of a thin-walled tube about 6 mm. wide and a glass rod about 2 mm. thick, elongated to act as a pointer. By suitable means a ring of the solid substance is deposited on the wall of the tube a short distance from the sealed end and the glass rod is rested on it. The melting-point is taken when the upper end of the pointer is seen to sink (Chem. Soc. Abstr. 1917, 112, ii. 192).

Fatty acids, waxes, and similar bodies are not easily introduced into capillary tubes, and in such cases Kuhara and Chikashigé (Chem. News. 1899, 80, 270) place a thin layer of the substance between microscope cover glasses suspended in a platinum foil support in a test-tube placed in the sulphuric acid bath. A modified method is described by Bunker (Pharm. J. 1909, [iv.] 28).

Air baths, which may be used at high temperatures instead of liquid baths, are described by Anschutz and Schultz (Ber. 1877, 10, 1800) and Kutscher and Otori (Zeitsch. physiol. Chem. 1904, 42, 193).

For a comparison of the different methods of procedure in the case of minute quantities of material, *see* Reinhardt (Zeitsch. anal. Chem. 25, 11).

The air thermometer has been adapted for use at extreme temperatures (Haase, Ber. 1893, 26, 1052; Meyer, Riddle, and Lamb, *ibid.* 1894, 27, 3129), but is less convenient than the thermo-element, for the application of which consult McCrae (Ann. Phys. Chem 1895, [2] 55, 95); Carrara and Coppadoro (Gazz. chim. ital. 1903, 33, i, 329); Guttmann (Chem. Soc. Trans. 1905, 87, 1037).

Stolzenberg (Ber. 1909, 42, 4322) has described two ingenious forms of apparatus for temperatures up to 350° and down to −60° respectively, which are similar in principle to that of Thiele, but the circulation is brought about not only by heating or cooling a spiral side tube, but also by bubbling dry carbon dioxide through it. For high temperatures, paraffin is used, and for low temperatures alcohol, the spiral being cooled in a Dewar flask with ether and solid carbon dioxide.

Slightly modified, it provides an accurate means of determining solubilities and (Chem. Zeit. 1910, 34, 66; Zeitsch. physikal. Chem. 1910, 71, 649) of measuring temperatures down to −140°, and is recommended as a low-temperature bath in physico-chemical laboratories. For further particulars and diagrams of apparatus, the original papers should be consulted.

A number of electrical methods have been devised, depending upon the completion of a circuit when the insulating coating of a substance on a platinum wire dipped in mercury melts (Löwe, Zeitsch. anal. Chem. 11, 211; Thierry, Arch. Sci. Phys. Nat. 1905, [iv.] 20, 59), or the breaking of a circuit when a wire connection in the case of metals (Loebe, Zeitsch. Elektrochem. 1907, 13, 592; Shukoff and Kurbatoff, J. Russ. Phys. Chem. Soc. 1907, 39, 1546; Jacquerod and Perrot, Arch. Sci. Phys. Nat. 1905, [iv.] 20, 28), or a bead connection in the case of borax and other glasses (Burgess and Holt, Proc. Roy. Soc. 1904, 74, 285) is broken on fusion, the temperature being ascertained by a thermo-element.

Burgess (Bureau Stand. Washington, 1907, 3, 345) describes an adaptation of the optical pyrometer to the determination of the melting-points of metals.

The melting-points of silicates are determined by Doelter by placing the finely powdered substance upon a small quartz plate heated in an electric resistance furnace, and observing with a microscope as the temperature is slowly raised (Zeitsch. Elektrochem. 1906, 12, 617).

A general account of melting-point methods at high temperatures is given by White (Amer. J. Sci. 1909, [iv.] 28, 453).

For the official method of determining melting-points in connection with the U.S. Pharmacopœia, *see* Menge (J. Soc. Chem. Ind. 1911, 30, 108).

For a method of determining melting-points by means of electric heating, *see* Malowan (Zeitsch. angew. Chem. 1919, 32, i. 16; Chem. Soc. Abstr. 1919, ii. 135; *cf.* Dana and Foote, Chem. and Mel. Eng. 1920, 22, 63).

The United States Bureau of Standards has published the following table of the melting-points of the chemical elements.

	°
Helium	<−271
Hydrogen	−259
Neon	−253(?)
Fluorine	−223
Oxygen	−218
Nitrogen	−210
Argon	−188
Krypton	−169
Xenon	−140
Chlorine	−101·5
Mercury	−38·87
Bromine	−7·3
Cæsium	+26
Gallium	30
Rubidium	38
Phosphorus	44
Potassium	62·3
Sodium	97·5
Iodine	113·5
Sulphur S_{I}	112·8
S_{II}	119·2
S_{III}	106·8
Indium	155
Lithium	186
Selenium	217–220
Tin	231·9
Bismuth	271
Thallium	302
Cadmium	320·9
Lead	327·4
Zinc	419·4
Tellurium	452
Antimony	630·0
Cerium	640
Magnesium	651
Aluminium	658·7
Radium	700
Calcium	810
Lanthanum	810(?)
Strontium	>Ca<Ba(?)
Neodymium	840(?)
Arsenic	850
Barium	850
Praseodymium	940
Germanium	958
Silver	960·5
Gold	1063·0
Copper	1083·0
Manganese	1230
Glucinum	1280
Samarium	1300–1400
Scandium	(?)
Silicon	1420
Nickel	1452
Cobalt	1480
Yttrium	1490
Iron	1530
Palladium	1549
Chromium	1615
Zirconium	1700(?)
Columbium	1700(?)
Thorium	>1700 <Mo
Vanadium	1720
Platinum	1755
Ytterbium	(?)
Titanium	1800
Uranium	>1850
Rhodium	1950
Boron	2200–2500
Iridium	2350(?)
Ruthenium	2450(?)
Molybdenum	2550
Osmium	2700(?)
Tantalum	2900
Tungsten	3400
Carbon	>3600

Those elements of which the melting-points are used as standard temperatures are printed in italics.

MELUBRIN. Trade name for mercury salicyl sulphonate.

MENDIPITE. A lead oxychloride $PbCl_2\cdot 2PbO$ found near Churchill on the Mendip Hills in Somersetshire. Crystallises in yellowish-white rhombic prisms; perfect prismatic cleavage; adamantine lustre, sp.gr. 7·1.

MENHADEN OIL is obtained from the body oil of the 'Menhaden fish' *Alosa menhaden*, Cuv. (*Brevoortia tyrannus*), a fish somewhat larger than a herring. From about May until November this fish appears in enormous quantities off the Atlantic coast of America (especially of New Jersey), so that as much as 400,000 tons of fish are caught in one season.

The fish are delivered from the steamers by means of elevators, on to automatic conveyors, from which they are passed over automatic scales into large boiling pans. These are provided with false bottoms, below which open steam coils are fixed. On boiling the contents of the pan, the fish are disintegrated and the oil separates easily from the flesh. After turning off the steam and allowing the mass to rest, the oil rises to the top and can be easily skimmed off by means of swivel skimmers.

During the last few years, 'boiling' vessels have been introduced which permit of continuous working, the fish being passed on conveyors through the boilers continuously, and exposed to the action of free steam. The time required for the fish to pass lasts from 15 to 20 minutes. The whole mass is then transported by screw conveyors into settling tanks, where the oil separates by gravitation. In either process, the 'fish scrap' falls to the bottom of the vessels, and is then pressed in hydraulic presses, similar to those used in the working up of 'tankage,' when a further quantity of oil, inferior in colour, is obtained. In some works, such pressed cake —termed 'chum'—is boiled out with hot water and pressed once more; but this process being unremunerative, except when the oil is very high in price, is not carried out in large works. The scrap is finally dried in continuous dryers, of which various types are in use (Anderson dryer, Cummer dryer, vacuum dryers), and is sold as a valuable manure. In fact, the 'scrap' was formerly considered as the main product, and it is owing to the demand for scrap that the fish oil industry has assumed such large dimensions. As the fish contain only from 1 to 16 p.c. of oil —rarely more—processes for its recovery from the scrap by means of solvents are most unlikely to prove remunerative, considering the enormous quantities of fish that must be dealt with.

With the extension of the industry, new uses have been found for the oil, which now not only ranks equal in value to the scrap, but has acquired a much higher price, especially at times when the price of linseed oil is very high.

The colour of menhaden oil varies in the first instance with the state of freshness in which the fish arrives, and in the second instance with the duration of the boiling process. The longer the oil has been allowed to remain in contact with the putrescible mass and the longer the fish has been boiled and hence the longer the oil has been in contact with the gluey water, the darker is its colour. Therefore, the separation of the oil from the gluey water is carried out as rapidly as possible. Fresh fish yield a light-coloured oil; the oil running from the 'scrap' in the presses is the darkest in colour.

In commerce the following three qualities are known: 'Prime crude,' 'Brown strained,' and 'Light strained oil.' Frequently the oils are differentiated into four grades—A, B, C, and D; A being extra pale, B pale, C brown, and D dark brown oil. Since the menhaden oil industry has extended along the Atlantic coast even down to Texas, the trade differentiates also between *northern menhaden oil* and *southern menhaden oil.* The process of refining consists mainly in brightening the oil by filtering, &c.

The light-coloured oils are allowed to rest some time in the cold, whereby 'stearine' separates; thus the 'winter oils' are obtained. They are then bleached by filtering over fuller's earth, &c.; in this manner two grades are obtained, viz. 'bleached winter white' and 'bleached winter' oils.

The sp.gr. of menhaden oil is 0·930 to 0·935. Freshly prepared menhaden oil has an iodine value reaching as high as 200 (Lewkowitsch). Most of the earlier analytical data contained in text-books must be corrected, especially as regards the iodine value, as those samples, the iodine values of which had been recorded, refer to oils which had undergone considerable oxidation on standing. Menhaden oil contains considerable amounts of clupanodonic acid. Thus the author obtained from specimens of pure menhaden oil as high a yield as 40 p.c. of clupanodonic octobromide.

The unsaponifiable matter consists chiefly of cholesterol, to the presence of which the slight optical activity of menhaden oil is due.

The principal use of menhaden oil is in the currying trade, and in the manufacture of sod oil. The oil is also employed in soap-making and for the tempering of steel. When linseed oil is high in price, menhaden oil is used to a considerable extent to adulterate it (to the detriment of the quality of the product) and, further, as a substitute thereof in the manufacture of varnishes, paint oils, and even linoleum. Menhaden oil is also used for adulterating Newfoundland cod-liver oil. J. L.

MENISPERMINE $C_{18}H_{24}O_2N_2$ (?), a crystalline alkaloid from *Anamirta Cocculus* (=*Menispermum Cocculus*), does not appear to have been examined since its discovery by Pelletier and Couerbe (Annalen, 1834, 10, 198).

MENOSAL. Menthyl salicylic methyl ester.

MENTHANTHONES *v.* KETONES.

MENTHENE *v.* CAMPHORS, TERPENES, PEPPERMINT.

MENTHENONE *v.* KETONES

MENTHOL *v.* CAMPHORS, PEPPERMINT.

MENTHONE *v.* CAMPHORS, PEPPERMINT.

MENTHOSPIRIN. Menthol ester of aspirin.

MENTHYL BORATE (*Estoral*) $BO(C_{10}H_{19})_3$.

MENTHYLETHOXYACETATE (*Coryfin*)

$$C_2H_5{\cdot}O{\cdot}CH_2{\cdot}COOC_{10}H_{19}.$$

MENTHYL ISOVALERATE (*Validol*)

$$C_4H_9{\cdot}COOC_{10}H_{19}$$

MENTHYL SALICYLATE (*Salimenthol*)

$$C_6H_4(OH)COOC_{10}H_{19}$$

MERCAPTANS (*Thiols*) are a group of substances derived from sulphuretted hydrogen in the same way as alcohol from water by the replacement of one hydrogen atom by an alkyl group. The mercaptans differ from alcohol in the same way that sulphuretted hydrogen differs from water; thus they have considerably lower boiling-points than the corresponding alcohols. They also possess one hydrogen atom replaceable by metal, but they are more acidic than the alcohols and form mercaptides of the heavy metals. The mercaptans were discovered by Zeise in 1833 (Annalen, 11, 2), and the name is derived from 'mercurio aptum,' owing to the formation of a characteristic mercury salt by the action of ethyl mercaptan on mercury oxide.

Formation.—General methods:

(1) By warming alkyl halides with potassium hydrogen sulphides in concentrated alcoholic solution.

$$R\boxed{X+K}SH=R{\cdot}SH+KX$$

(where R=alkyl, X=halogen).

(2) By heating alcohols or phenols with phosphorus pentasulphide

$$5ROH+P_2S_5=5R{\cdot}SH+P_2O_5$$

(3) By distilling a solution of potassium alkyl sulphate with potassium hydrogen sulphide.

$$R\boxed{OSO_3K+K}SH=R{\cdot}SH+K_2SO_4$$

They are also formed in the reduction of thiocyanic esters, $CNS{\cdot}R+2H=HCN+HSR$.

(4) By the action of sulphuretted hydrogen on the alcohol vapour at 300°–350° in presence of anhydrous thoria (ThO_2) (Sabatier and Mailhe) *e.g.* $C_2H_5{\cdot}OH+H_2S=C_2H_5{\cdot}SH+H_2O$.

Cf. Kramer and Reid, J. Amer. Chem. Soc. 1921, 43, 880.

(5) By reduction of disulphides by dextrose (Claasz. Ber. 1912, 45, 2424).

(6) By treating a mixture of the alcohol, red phosphorus, sodium sulphate and sodium

sulphide with bromine. This method which gives yields of 50–60 p.c. is based on the reactions:

(1) $3R\cdot OH+3Br+P=3RBr+H_3PO_3$.
(2) $4H_3PO_3+Na_2SO_4=Na_2S+4H_3PO_4$.
(3) $Na_2S+H_3PO_4=Na_2HPO_4+H_2S$.
(4) $RBr+H_2S=R\cdot SH+HBr$.

(Mereshkovski, J. Russ. Phys. Chem. Soc. 1914, 46, 1082.)

Aromatic mercaptans can be obtained by acting on the diazo-aromatic compounds with potassium ethyl xanthate and decomposing the compound thus formed with caustic alkali (Lenhart, J. pr. Chem. [ii.] 41, 179; Bourgeois, Rec. trav. chim. 1899, 18, 426); by the reduction of the chloride of the sulphonic acid derivative, and by the electrolytic reduction of the thiochlorides or their nitro derivatives in sulphuric acid solution using lead electrodes and keeping the anode liquid at 20° (Fichter and Bernoulli, Ber. 1909, 42, 4308).

Mercaptans of the anthracene series are obtained by heating together the halogenated anthraquinones and the alkali sulphides or hydrosulphides (D. R. P. 204772, 208640; Frdl. 1908–10, 20)

Mercaptans of the anthraquinone series are obtained in the following manner: 10 kilos. of anthraquinone-*α*-thiocyanate are made into a paste with 20 litres of alcohol and boiled under a reflux condenser with 60 litres of a 10 p.c. sodium hydroxide solution until the product forms a clear cherry-red solution in water. Hot water is now added until the whole product is dissolved, and after filtration the mercaptan is precipitated by addition of hydrochloric acid containing a little sulphurous acid (D. R. P. 208640, 1907; 212857, 1909; J. Soc. Chem. Ind. 1909, 469).

Mercaptans yielding dyes with diazo compounds can be obtained by heating sodium naphthalene-*β*-sulphonate and a 50 p.c. solution of potassium hydrosulphide for 3 hours at 200°–220° under a pressure of 10–12 atmospheres in an iron vessel. The product is then treated with dilute hydrochloric acid and extracted with ether. The disulphide which remains undissolved can also be converted into the mercaptan by heating with potassium hydrosulphide and alcohol. When benzene sulphonic acid and *m*-disulphonic acid are similarly treated, coloured products having the odour of mercaptans are formed (Schwalbe, Ber. 1906, 39, 3102).

Properties.—The mercaptans are mostly liquids insoluble in water, soluble in alkalis and, particularly the lower, more volatile ones, have a very characteristic disagreeable odour, their smell being indeed a far more delicate test than any of their chemical reactions. Like hydrogen sulphide they are readily oxidised by oxidising agents and even by air, forming disulphides $2R\cdot SH+O=RS\cdot SR+H_2O$. When oxidised with nitric acid they form sulphonic acids

$$R\cdot SH+O_3=RSO_3H$$

Mercaptans condense with nitriles thus:

$$RSH+R'CN=NH:CR'\cdot SR$$

Thus by the action of ethylene cyanide on ethylene sulphhydrate, *succiniminodithioethylene ether* $(CH_2C(NH)\cdot S\cdot CH_2)_2$ is formed, the hydrochloride of which is an amorphous dark green powder soluble in water; the solution dyes wool and silk a bright green, fast to light but turning yellow (owing to the liberation of the free base) when treated with alkalis (Autenrieth and Brüning, Ber. 1903, 36, 3464).

The alkyl mercaptans and their derivatives react in general with acid chlorides to form esters of the corresponding thio acids thus:

$$3RSH+PCl_3=P(SR)_3+3HCl$$

or $(COCl)_2+Pb(SC_6H_5)_2=(CO\cdot S\cdot C_6H_5)_2+PbCl_2$. The final products of the reaction, however, depend on the stability of the ester formed, or, if it is unstable, on the manner of its decomposition. When treated with hot potassium hydroxide solution, the stable esters are converted into the mercaptide, whilst with alcoholic potassium hydrosulphide they yield potassium thio salts (Jones and Tasker, Chem. Soc. Trans. 1909, 1904).

With sulphuryl chloride, the mercaptans react thus:

$$8RSH+4SOCl_2=8HCl+2SO_2+3(R\cdot S)_2+R_2S_4$$
$$\text{and } 4RSH+SOCl_2=(R\cdot S)_2+R_2S_3+H_2O+2HCl$$

which reaction preponderates depending on the conditions of the experiment (Jones and Tasker, *l.c.* 1910). The reaction of mercaptans with nitrosyl chloride and with thionylaniline is similar to that with sulphuryl chloride. When nitrosyl chloride is added to a mercaptan, the latter absorbs it, forming a rich cherry-red coloured solution which rapidly evolves nitric oxide and finally loses its colour. In a freezing mixture of solid carbon dioxide in ether, however, hydroxylamine hydrochloride is formed (Jones and Tasker, *l.c.*; Holmberg, Ber. 1910, 43, 226).

Mercaptans combine with aldehydes in the presence of hydrogen chloride, forming *mercaptals*, $R\cdot CH\overline{O+2H}SR'=R\cdot CH(SR')_2$ (Baumann, Ber. 1885, 18, 883; Blanksma, Rec. trav. chim. 1901, 20, 399). They are insoluble in water, stable in the cold but readily decomposed on warming.

Mercaptans combine with certain sugars in cooled hydrochloric acid solution, forming mercaptals (Fischer, Ber. 1894, 27, 673).

Glucose ethyl mercaptal $C_6H_{12}O_5(SEt)_2$ forms slender colourless needles or thin plates, m.p. 127°–128°, $a_D-29{\cdot}8°$ at 50°. It has a bitter taste and decomposes on distillation, yielding a product with an odour of roasted onions. A number of other similar mercaptals are described by Fischer.

Similarly, the mercaptans condense with ketones, forming *mercaptoles*

$$R_2C\overline{O+2H}SR'=R_2C\cdot(SR')_2+H_2O$$

(Baumann, *l.c.*; Posner and Fahrenhorst, Ber. 1899, 32, 2749; Blanksma, *l.c.*), and the latter, on oxidation, yield disulphones.

The nature and stability of the mercaptoles and disulphones formed by the interaction of ketonic esters and the mercaptans depend both on the nature of the ester and of the mercaptan (Posner, Ber. 1901, 34, 2643).

α-, *β*-, or *γ*-Diketones containing both carbonyl groups attached to methyl radicles, readily react with four molecules of a mercaptan yielding dimercaptoles which on oxidation yield tetrasulphones. If, however, one of the carbonyl groups of the diketones is attached to a substituted methyl group, the ketone reacts with only two molecules of a mercaptan forming a ketomercaptol which on oxidation gives a keto-disulphone. A number of these products are described by Posner (Ber. 1900, 33, 2983).

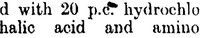
In the presence of hydrochloric acid, the mercaptans react with unsaturated ketones, forming both addition and condensation products (Posner, Ber. 1902, 35, 799; 1904, 37, 502; *see* also Fasbender, Ber. 20, 460); but if piperidine or sodium ethoxide is employed as catalytic agent instead of hydrogen chloride, only additive products are obtained (Ruhemann, Chem. Soc. Trans. 1905, 17, 461; Proc. Roy. Soc. 1904, 251). The number of mercaptan groups uniting with a diolefinic ketone also depends on the nature of the catalytic agent. The mercaptans also combine with many unsaturated hydrocarbons and acids (Posner, Ber. 1905, 38, 646; *ibid.* 1907, 40, 4788).

According to Stadler (Ber. 1884, 17, 2075), the mercaptans of the aliphatic series react with diazo compounds yielding explosive substances.

Ethyl mercaptan (mercaptan), produced technically by the interaction of ethyl chloride and potassium hydrogen sulphide, is a sparingly soluble liquid with a very disagreeable smell, b.p. 36·2°, sp.gr. 0·83907 at 20°/4° (*v. Ethyl sulphydrate*, art. ETHYL). It may be formed synthetically by passing hydrogen sulphide through a solution of aluminium bromide in ethyl bromide and treating the $AlBr_3{\cdot}EtBr,H_2S$ (snow-white crystals, m.p. 81°) with water (Plotnikov, J. Russ. Phys. Chem. Soc. 1913, 45, 1162). It is also produced by the action of yeast or zymase solution on thioacetaldehyde (Neuberg and Nord). It combines with acetone, forming dimethyl diethyl mercaptole, which when oxidised with potassium permanganate yields diethyl sulphomethyl methane (acetone-diethyl sulphone) $Me_2C(SO_2Et)_2$. The latter crystallises in colourless prisms, m.p. 126°, is sparingly soluble in water and is employed in medicine, under the name 'sulphonal,' as a soporific. Trional $MeEtC(SO_2Et)_2$, m.p. 75°, and tetronal $Et_2C(SO_2Et)_2$, m.p. 85°, are prepared similarly and are also used in medicine (*v.* TETRONAL AND TRIONAL).

Ethyl mercaptan has no action on anthraquinone or phenanthraquinone, but it reacts with quinone forming quinol, quinhydrone, and thioaldehyde and under certain conditions it forms a red crystalline compound in which two hydrogens in the quinone nucleus are substituted by SEt groups (Tarbouriech, Bull. Soc. chim. 1901, [iii.] 25, 313; Sammis, J. Amer. Chem. Soc. 1905, 27, 1120).

Ethyl mercaptophthalimide



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}N(CH_2)_2SH$$

becomes plastic at 76° and melts at 79°–80°. When boiled with 20 p.c. hydrochloric acid it yields phthalic acid and aminomercaptan hydrochloride $NH_2C_2H_4SH,HCl$ (Gabriel, Ber. 1891, 24, 1110, 3098).

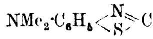
Phenyl mercaptan has b.p. 169·5°; *p-tolyl mercaptan*, b.p. 195°; *m-tolyl mercaptan*, b.p. 195·5°; and *β-naphthyl mercaptan*, b.p. 288° (Bourgeois, *l.c.*; Autenrieth and Geyer, Ber. 1908, 41, 4256).

p-Tolylaminoanthraquinone mercaptan

$$C_7H_7NHC_{14}H_6O_2SH$$

forms dark blue needles and yields on sulphonation a violet wool dye (D. R. P. 206536, 1909).

Anhydroformaldehyde dimethyl-p-phenylenediamine mercaptan (*5-dimethylamino-2-methyleneaminophenyl mercaptan*) $SHC_6H_3(NMe_2)N:CH_2$ is formed by treating *as*-dimethyl-*p*-phenylenediamine thiosulphonic acid dissolved in aqueous ammonia, with formaldehyde and hydrochloric acid. It rapidly polymerises and is isolated as the ferrocyanide $3C_9H_{12}N_2S,2H_4Fe(CN)_6,5H_2O$. When the freshly prepared mercaptan is treated with sodium nitrite and hydrochloric acid it yields 5-dimethylaminobenzthiazole

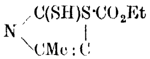


$$NMe_2{\cdot}C_6H_3{<}\begin{matrix}N\\S\end{matrix}{\gg}CH$$

m.p. 73°–74° (Schmidt, Ber. 1906, 39, 2406).

Mercaptothiazoles are prepared by the condensation of α-halogenated ketones with ammonium dithiocarbamate (Miolati, Gazz. chim. ital. 23, i. 575)

Ethyl methyl mercaptothiazolecarboxylate



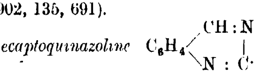
$$N\begin{matrix}\diagup C(SH)S{\cdot}CO_2Et\\ \diagdown CMe:C\end{matrix}$$

melts at 141°, and is soluble in alcohol and ether but not in water; the free acid has m.p. 211°–212°.

Methylmercaptothiazole melts at 89°–90° and is soluble in organic solvents. *Phenyl mercaptothiazole* melts at 168°.

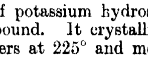
For a number of mercaptothiazoline derivatives, *see* Hirsch (Ber. 23, 964); Kahan (*ibid.* 1897, 30, 1318); Gabriel and Leupold (*ibid.* 1898, 31, 2837); Janecke (*ibid.* 1899, 32, 1103); Straus (*ibid.* 1900, 33, 2830).

Mercaptogalactoxazoline



$$N\begin{matrix}\diagup CH_2{\cdot}CH(CH{\cdot}OH)_3CH_2{\cdot}OH,\\ \diagdown CSH{\cdot}O\end{matrix}$$

m.p. 185°–186°, is formed by heating galactamine with carbon disulphide. Like the corresponding dextrose derivative it gives a crystalline compound with silver nitrate (Roux, Compt. rend. 1902, 135, 691).

2-Mecaptoquinazoline  $C_6H_4\begin{matrix}\diagup CH:N\\ \diagdown N:C{\cdot}SH\end{matrix}$, is prepared by the action of potassium hydrosulphide on the chloro compound. It crystallises in hexagonal plates, sinters at 225° and melts at 229°–231° (Gabriel, Ber. 1903, 36, 800). Mercapto oxazoline derivatives are described by Maquenne and Roux (Compt. rend. 1902, 134, 1589).

Many other mercaptan derivatives have been prepared (Baumann, Ber. 1885, 18, 891; Jacobson, *ibid.* 1887, 20, 1895; *ibid.* 1888, 21, 2624; Klason, *ibid.* 20, 3409; *ibid.* 28, ref. 942; Freund, *ibid.* 1896, 29, 2483; Brjuchonenko, J. pr. Chem. [ii.] 59, 46, 596; Eibner, Ber. 1901, 34, 657; Freund and Bamberg, *ibid.* 1902, 35, 1753; Posner, *ibid.* 799; de Jong, Rec. trav. chim. 1902, 21, 295; Autenrieth and Geyer, Ber. 1908, 41, 4249, 4256; Pollak, Monatsh. 1914, 35, 1445, 1467; Rennert, Ber. 1915, 48, 459; Pollak and Schadler, Monatsh. 1918, 39, 129; Pollak, von Fielder and Roth, *idem*, 179)

Mercaptides are formed by the action of the metal on the mercaptan (as in the case of the alkali salts) or by the interaction of an alcoholic solution of the mercaptan with the oxide or acetate of the metal.

Many such crystalline compounds are known. They are mostly decomposed by mineral acids, with liberation of the mercaptan, and react with alkyl halides forming thio ethers, thus:

$$\mathrm{RS|Na+I|R'=R{\cdot}S{\cdot}R'}$$

(Otto, J. pr. Chem. 1895, [ii.] 51, 285). With ethyl α-chloroacetoacetate they yield alkyl sulphide and ethyl diacetyl succinate:

$$\mathrm{2RSNa+2CMeO{\cdot}CHCl{\cdot}CO_2Et = 2NaCl+R_2S_2+(CHAc{\cdot}CO_2Et)_2}$$

(Finger and Hemmeter, J. pr. Chem. 1909, 79, 449). The mercaptides react with mustard oils, forming dithiourethanes:

$$\mathrm{RNCS+R'SNa = R{\cdot}N:CSNa{\cdot}SR' \xrightarrow{HCl} NaCl+RNH{\cdot}CS{\cdot}SR'},$$

and this is suggested by Roschdestvensky as a good method of identifying the mercaptans (J. Russ. Phys. Chem. Soc. 1909, 41, 1438).

Mercury mercaptide $(\mathrm{EtS})_2\mathrm{Hg}$ crystallises in white leaflets. With mercuric chloride, however, ethyl mercaptan forms a sparingly soluble double salt, EtS·HgCl. Similar iodide and bromide compounds are also known (*cf.* Rây, Chem. Soc. Trans. 1919, 871.

Mercapturic acids are hydroxycarboxylic acids in which the hydroxyl group is replaced by an SH group (Carius, Annalen 124, 43; Claesson, Ber. 1877, 1346; Friedmann, Beitr. Chem. Physiol. Path. 1903, 4, 486).

Mercaptal acids are obtained by the condensation of aldehydes with thiol acids (Holmberg and Mattisson, Annalen, 1907, 353, 123).

Selenium and tellurium form compounds corresponding with the mercaptans and having a similar offensive smell.

MERCERISING. Mercerising or 'lustreing' consists in impregnating cotton fibres with concentrated caustic soda lye, either with or without the application of tension, and in stretching the material before and during the removal of the soda by means of washing.

John Mercer noticed in 1844 that cotton fabrics, when immersed in concentrated soda lye, became transparent and that a considerable swelling and shrinkage of the fibres occurred. He also found that the soda could be readily removed by washing with water and that the fibres afterwards again became opaque and exhibited increased affinity for a number of dyestuffs. The fact that concentrated caustic soda lye causes the cotton fibre to contract seems, however, to have been known in France at the time when Mercer made his discovery (J. Hübner, J. Soc. Dyers and Col. 1911, 27). The treatment briefly described above was patented by Mercer in 1850. About the same time, he applied his discovery to the 'crimping' of cotton fabrics, by printing stripes upon the fabric with thickened concentrated caustic soda lye, with the result that the portions printed upon became contracted, whilst the parts which had not been acted upon by the soda became drawn together or 'crimped.'

It has been suggested that 'hydrated cellulose' is the result of mercerisation, but although mercerised cellulose contains more water in the air-dry condition than ordinary cellulose, C. G. Schwalbe (Zeitsch. angew. Chem. 20, 2172, 1907) and H. Ost and F. Westhoff (Chem. Zeit. 33, 197, 1907) state that they have not been able to prove that mercerised cellulose contains chemically combined water. It should also be pointed out that the excess of water contained in mercerised cotton can be readily removed by drying (J. F. Copley, J. Soc. Dyers and Col. 24, 72); by the application of heavy pressure after mercerising, whilst the material is still in the wet state (J. Hübner, Eng. Pat. 12455); by extraction with absolute alcohol (J. Hübner and F. Teltscher, J. Soc. Chem. Ind. 1909, 28, 641) and by drying at ordinary temperature over calcium chloride or phosphorus pentoxide.

In 1889, H. A. Lowe observed that if a cotton fabric is prevented from contracting during treatment with concentrated caustic soda lye and subsequent washing it acquires a silk-like lustre (Eng. Pat. 20314). Lowe allowed his patent rights to lapse and in 1895 Thomas and Prevost patented the same process in Germany (Ger. Pat. 85564). This patent was, however, ultimately annulled.

Mercer had already noticed that effects, similar to those obtained by caustic soda, could be produced by the application of sulphuric acid, phosphoric acid, and zinc chloride. Soon after the publication of Thomas and Prevost's patent, a large number of patents of doubtful value were taken out in order to protect the application of various mercerising agents. The fact that a superior lustre could be obtained on the long-stapled Sea Island and Egyptian cottons was also made the subject of a patent (*see* Gardner, Die Mercerisation der Baumwolle).

Knecht (J. Soc. Dyers and Col. 1896, 12, 89) found that cotton could be mercerised by treating it with nitric acid of 83° to 84°Tw., and J. Hübner and W. J. Pope (J. Soc. Chem. Ind. 1903, 22, 70) discovered that saturated solutions of iodides produce a similar effect. A saturated solution of barium-mercuric iodide produces practically the same degree of shrinkage and increased affinity for dyestuffs as concentrated caustic soda lye.

Mercer pointed out that soda lye of as low a strength as 20°Tw., produces a distinct effect on the cotton fibre, and it had been commonly accepted that lyes below this strength exerted practically no action on the fibres. Hübner and Pope (J. Soc. Chem. Ind. 1904, 23, 404), however, found that a lye of only 1°Tw. concentration appreciably increases the affinity of the cotton fibre for the substantive dyestuffs and produces a certain degree of shrinkage. They also showed that the degree of shrinkage is not directly proportionate to the concentration of the lye used, and that maximum shrinkage is produced by a soda lye of about 45°Tw., whilst the shrinkage again decreases if the strength of the lye is increased above 45°Tw.

This supplied an explanation of the fact that cotton yarn and cloth, after treatment under tension with soda lye of 60° to 70°Tw., are frequently torn on the mercerising machine during the first stages of washing.

It had been generally assumed that a mercerising agent, in order to produce lustre on the fibre, must exert a shrinkage and swelling action. Hübner and Pope (*l.c.*) observed that the agent must also be capable of untwisting the naturally twisted cotton fibre.

This, coupled with the fact that single cotton fibres (Fig. 1) are twisted in parts to the right and in parts to the left, several changes in the direction of the twist being noticeable in a single fibre, affords a rational explanation of the production of lustre in mercerising. As a result of the untwisting of these different twists during mercerisation under tension, during which operation the fibres are firmly held by the twist of the yarn, the original ribbon-like twisted fibre becomes converted into a straight rod, of nearly circular cross-section, which carries on its surface smooth elevations in the shape of rounded ridges, which reflect the light falling on them from any direction (Fig. 2). Maximum lustre can, therefore, only be obtained if the mercerising agent is capable of producing shrinking, swelling, and untwisting of the fibres in a high degree. Waterglass, glycerol, common salt, if added to the caustic soda lye used in mercerising, diminish the extent of the swelling and the shrinking of the fibres, the lustre obtained is, therefore, inferior to that produced by caustic soda alone. Sodium sulphide, nitric acid, and hydrochloric acid, which cause untwisting of the fibre, accompanied, however, with but little shrinking and swelling, give still less lustre, whilst barium-mercuric iodide, which produces maximum swelling and shrinking but no untwisting, produces practically no lustre.

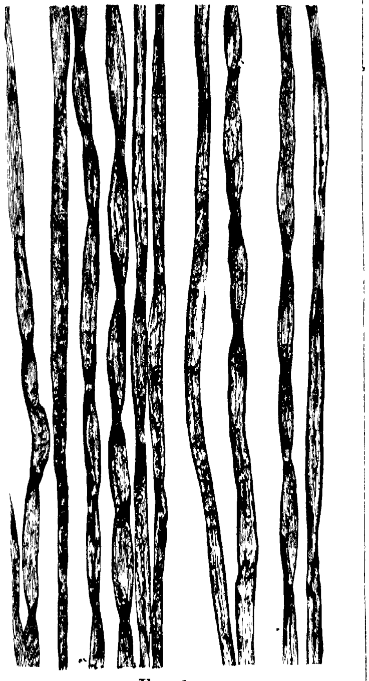


FIG. 1.

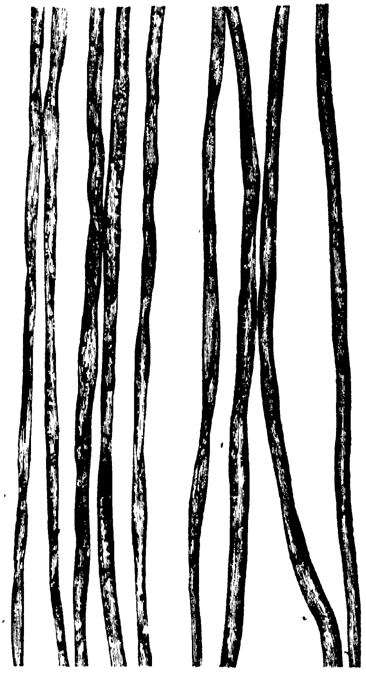


FIG. 2.

Gladstone (J. Chem. Soc. 1853, 5, 17) suggested that in mercerising a definite chemical compound, 'soda cellulose' $(C_6H_{10}O_5)_2NaOH$, is formed, which decomposes readily on treatment with water. J. Hübner and F. Teltscher (J. Soc. Chem. Ind. 1909, 28, 614) have shown that the existence of such a definite compound is very doubtful and that the amount of soda retained by the cellulose after extraction with absolute alcohol is much smaller than that given by Gladstone.

The dyeing properties of mercerised cellulose have been studied by a number of investigators. R. Haller (Zeitsch. Farb. und Textilchemie, 1907, 8, 125) assumes that the soda lye removes the cutinised layer from the fibres, thus exposing pure cellulose, which is capable of absorbing dyestuffs more readily.

In order to thoroughly mercerise the fibres, the material must be allowed to remain in contact with the soda lye for about ½ to 1 minute. Although it is the practice in some works to allow the material to remain for a considerable time in contact with the soda lye after impregnation, and before stretching and washing, the results obtained are in no way superior to those obtained when working continuously.

Uniform results in mercerising can only be obtained if the soda lye used is kept at uniform strength and temperature. Special refrigerating machines are frequently employed for cooling the soda lye.

Doubled yarns, made of long-stapled Sea Island or Egyptian cotton, give the most brilliant results in mercerising, but good results can also be obtained on yarns spun from combed American cottons. Single yarns cannot be successfully mercerised on account of the twist being too weak to resist the shrinking of the fibres. The best results in mercerising cotton fabrics are obtained on face cloths, such as sateens, Italian linings, &c. A considerable change in the structure of the fabric takes place during mercerisation (J. Hubner, J. Soc. Dyers and Col. 1911, 27, 128).

The removal of all loose fibres from the surface of the material by careful singeing leads to an increase of the lustre of the mercerised fabric.

Cotton yarn is usually mercerised after it has been boiled in the kier, whilst cotton fabrics are sometimes only scoured before mercerising. More frequently the fabrics are mercerised after the first 'boil' in the kier, or in some cases after they have been bleached ('chemicked'). Cotton in the loose state, as it comes from the bale, cannot be successfully mercerised.

A number of methods have been suggested for mercerising cotton in the state of 'sliver,' but none of these methods has, so far, found any extensive practical application.

No satisfactory lustre can be produced by treating cops or 'cheeses' (cross-wound spools) with caustic soda lye; but cotton yarn in the hank is very largely and successfully mercerised. Automatically working machines are used for this purpose, in which the yarn is stretched, by subjection to tension, over heavy iron rollers, both during impregnation with the lye and during washing.

Cotton warps can be mercerised in a machine resembling the ordinary warp-dyeing machine. The warp is usually impregnated with the soda lye in the first two compartments, while it is washed free from soda in the other compartments. Provision should be made in order to allow each successive set of squeezing rollers to be run at a slightly higher speed. In some cases, warps are mercerised in a machine resembling the 'warp slasher.'

Although a great variety of machines have been invented and used for mercerising cotton piece goods, machines in which the fabric after impregnation is stretched on a 'clip stenter,' are now chiefly employed. A complete mercerising range consists of a padding mangle, the stenter with washing arrangement and the necessary washing, souring, and washing cisterns. In the padding mangle, the cloth is usually twice impregnated with the caustic soda lye and squeezed after each impregnation between cast iron and indiarubber bowls. The trough containing the lye is often provided with an outer cavity to which ice may be supplied or through which refrigerated brine may be circulated in order to keep the lye at a low and uniform temperature. After impregnation, the cloth passes usually directly on to the stenter in which the edges are seized and held by two endless chains of clips, which travel along each side of the stenter. The end of the stenter at which the cloth enters is tapered and thus the fabric is gradually stretched out to its 'grey width,' after which the chains run parallel to the delivery end. While on the stenter the caustic soda is removed by showering hot water on the cloth. The economy of recovery of the caustic being of importance, it is customary, in order to obtain a wash-water containing a high percentage of caustic soda, to conduct the washing on the counter-current principle.

For this purpose three or more sets of spirt pipes are provided, clean hot water being introduced into the first set of pipes, which are placed nearest the delivery end of the machine, whilst the same water is then used successively in the other sets. The cloth is ultimately released from the clips and passed through a number of tanks containing hot water and weak acid and passes finally through a washing machine.

With a view to ensure complete penetration of cotton fabrics when mercerising at a high speed, Mather and Platt have introduced a mercerising plant in which the fabric, after having been impregnated in the mangle, is conducted over a number of iron drums, from which it passes into a second impregnating mangle, before being conducted on to the stentering frame.

Krais has patented an arrangement by means of which the soda lye is forced out of the cloth by blowing steam against it.

In order to enable the soda lye to be used over again, the washwaters are concentrated in multiple-effect evaporators and ultimately treated with caustic lime.

Reactions for the characterisation of mercerised cotton.—Although thoroughly mercerised cotton fibres exhibit very specific microscopic characteristics (see Fig. 2), it is exceedingly difficult in many instances to decide with certainty whether goods have been mercerised or not, because the fibres have frequently only been incompletely penetrated by the soda lye. The following chemical reactions (J. Hübner, J. Soc. Chem. Ind. 1908, 27, 105) may be used in order to ascertain whether cotton has been treated with caustic soda lye.

1. If dark-coloured samples have to be tested, it will be necessary to first discharge the colour and to completely remove any starch which may be present. The sample should then be squeezed between filter-paper and immersed for a few seconds in the following solution: 20 grams iodine dissolved in 100 c.c. of a saturated solution of potassium iodide. If a non-mercerised sample is immersed along with a mercerised one and if, after removal from the iodine solution, both samples are washed repeatedly in water, it will be noticed that the non-mercerised cotton becomes white, whilst the mercerised sample remains of a bluish-black colour, which only fades very slowly on prolonged washing.

2. Two solutions are prepared, (*a*) containing 280 grams of zinc chloride in 300 c.c. of water and (*b*) 1 gram of iodine, 20 grams of potassium iodide, 100 c.c. of water. The reagent is prepared by adding about 10 drops of (*b*) to 100 c.c. of (*a*). A mercerised pattern, immersed in this solution for about 20 minutes, turns a dark reddish-blue, whilst non-mercerised cotton remains practically white.

By immersing samples which have been mercerised with known strengths of caustic soda along with the one under examination, it is possible, by comparing the depth of coloration of the samples, to ascertain, with a certain degree of accuracy, the strength of caustic soda which has been employed in mercerisation.

J. Hü.

MERCURIC FULMINATE *v.* Fulminic acid; also Explosives.

MERCURIOCOLOLEO. Double. oleate of chlolesterol and mercury.

MERCUROCHROME. The disodium salt of dibromoxymercuryfluorescein used as an antiseptic for the genito-urinary tract. Iridescent green scales or granules, odourless and permanent in the air. Freely soluble in water, soluble in dilute alcohol, insoluble in chloroform or ether. Does not precipitate proteins and does not give the usual tests for mercury. Gives with hydrochloric acid an orange-red precipitate. The solution stains the skin red. The free acid is a red powder insoluble in water but readily soluble in sodium hydroxide solution with a deep cherry-red colour showing fluorescence on dilution.

MERCUROL, MERCURIOL, MERCOCHINOL, MERGOL, MERIODIN *v.* Synthetic drugs.

MERCUROPHEN. Trade name for oxymercuri-*o*-nitrophenoxide, an odourless, brick-red powder, used as an antiseptic. Has a lower toxicity than mercuric chloride, but is much more active as a germicide.

MERCURY. Quicksilver. (*Mercure*, Fr: *Quecksilber*, Ger.) Sym. Hg. At.w. 200·63 (Easley and Brann); 200·37 (Taylor and Hulett); 200·57 (Baker and Watson).

Ores. *Native mercury* occurs as a decomposition product of cinnabar in the upper portions of the deposits of that mineral. The mercury is usually disseminated through the ore in the form of minute globules which sometimes collect in cavities in the rock. In California, native mercury disseminated through serpentine or in detritus has been found near the outcrops at the Sonoma mine, Rattlesnake mine, &c., associated with mere traces of cinnabar. At greater depths the ore is always cinnabar alone (Egleston's Metallurgy of Silver, Gold, and Mercury in the United States, ii. 801).

Native amalgam containing about 70 p.c. of silver is found in crystals belonging to the cubic system at Arqueros, near Coquimbo, at Moschellandsberg in the Rhine provinces and elsewhere Native calomel (*horn mercury*) HgCl occurs at Idria and Almaden, and selenide, sulphoselenide (*onofrite*), and other compounds of mercury have also been found in small quantities in various localities. Oxychlorides of mercury (*terlinguaite*, *eglestonite* and *montroydite*) occur with cinnabar in Texas.

Cinnabar HgS is the only ore which is regularly worked for mercury. It is dimorphous. The red variety, cinnabar proper, occurs in rhombohedral crystals, but is usually found massive or earthy, intermixed with quartz, sandstone, schists, bituminous substances, iron pyrites, &c. It is distinguished by its red colour and scarlet streak. Its hardness is 2·5 and its specific gravity 8·1. When intermixed with bituminous substances which give it a dark colour, it is known as hepatic cinnabar. Cinnabar occurs in eruptive rocks and in sedimentary rocks of all ages. Meta-cinnabarite is a black variety of cinnabar with a black streak It occurs in tetrahedral crystals but is usually massive, associated with cinnabar. Its hardness is 3 and its specific gravity 7·8. (Quicksilver, 1913–1919, Imperial Mineral Resources Bureau)

The chief deposits are at Almaden in Spain, at Idria in Carniola, at Monte Amiata in Tuscany, and at New Idria, and other localities in California. There are also deposits in Texas, Nevada, Mexico, the Carpathian mountains, Russia, China, Asia Minor, and in other countries.

The famous Almaden mines in Spain were known to Theophrastus, 315 B.C., as furnishing cinnabar to the Greeks, and they were afterwards worked by the Romans. The cinnabar permeates or occurs as pockets in thick veins of quartz inclined at a high angle and contained in Silurian slates (Phillips' Ore Deposits, 374). The ore contains bituminous matter and iron pyrites. Native mercury accumulates in the numerous clefts and cavities in the deposit. The richest ore contains about 25 p.c. of mercury, and the mean yield of the ores, worked in 1918, was 6·5 p.c. (Quicksilver, 1913–1919. Imperial Mineral Resources Bureau).

At Idria the sulphide occurs as a dark red slaty deposit contained in veins or disseminated in triassic shales and limestones. Some hepatic cinnabar occurs and also *korallenerz* or coral ore, which contains calcium phosphate (Phillips, *l.c.* 329; Lipold, Oesterr. Zeitsch. 1882, 30, 84). The mines were discovered in 1490 and have been in the hands of the Government since 1580. The ore varies in grade from *stahlerz*, containing 75 p.c. mercury, down to ores containing 0·2 p.c., the average being about 1·1 p.c.

At Monte Amiata, cinnabar occurs as segregations in Eocene formations. These deposits were exploited by the ancient Etruscans and again in the Middle Ages. The present operations were begun at Siele in 1846. The average amount of quicksilver contained in the ores was 0·8 p.c. in 1908. The output has risen from 173 tons in 1898 to 1303 tons in 1920 (Spirek, Zeitsch prakt. Geol. 1897, 369; Schnabel and Louis' Metallurgy, 2nd ed. ii. 335; C. de Castro, Le Miniere di Mercurio del Monte Amiata; Quicksilver, 1913–1919).

At Nikitowka, the ore consists of sandstone of carboniferous age impregnated with cinnabar. In 1906, the yield of mercury was only 0·28 p.c. and the production fell from 616 tons of mercury in 1897 to 47 tons in 1908. The deposits were worked by the ancient Greeks, and after a lapse of 2000 years operations were begun again in 1886 (Schnabel and Louis, *l.c.*), but have been trifling in extent since 1912.

In California cinnabar occurs disseminated through a zone of slates, serpentine, sandstones, and limestones of Cretaceous and Jurassic age. Some rich ore occurs, especially where serpentine and sandstone are in contact, but the average yield is now under 0·4 p.c., although it was 36 p.c. in 1850 with a similar output. The deposits were known to the Indians, who used the cinnabar as paint, but the mines were first worked systematically in 1845. The most important mines are New Idria and New Almaden, but the latter now yields very little, being almost exhausted.

Mercury also occurs as a sulphide in ores of other metals. The *mercurial fahlore* (*see* Fahlore) of Hungary contains up to 17 p.c. of mercury. At Kotterbach this fahlore occurs in spathic iron ores (Schnabel and Louis, *l.c.* ii. 438). According to Bellingrodt (Chem. Zeit. 1886, 10, 1039), zinc blende roasted at Oberhausen contains 0·2 p.c. of mercury which is extracted as a by-product. Zinc ore is also treated for mercury at the Taghit mine, Algeria (Min. Ind. for 1902, 11, 548). At Nipissing, Cobalt, Ontario, silver ore occurs containing from 2-5 lbs. mercury per ton, chiefly in the form of native amalgam (Eng. and Ming. Jour. Dec. 7, 1912, 1078).

Extraction from ores. There are two methods of extracting mercury from cinnabar suitable for use on a large scale:—

1. By heating cinnabar in air, the action being represented by the equation

$$HgS+O_2=Hg+SO_2$$

2. By heating cinnabar with lime or iron, air being excluded. The chemical action may be represented by the equations

$$4HgS+4CaO=4Hg+3CaS+CaSO_4$$
$$HgS+Fe=Hg+FeS$$

In each of these cases, the temperature necessary for the reaction is higher than the boiling-point of mercury, so that the latter is volatilised and has to be condensed. In the air roasting process, the mercurial vapours are mixed with a large volume of sulphur dioxide, nitrogen, carbon dioxide, and other gases, and condensation is difficult. Nevertheless, the roasting process is now generally used, partly owing to the high cost of retorting with lime or iron, which prohibits the use of that method for poor ores, but mainly on account of the injury to the health of the workmen by the concentrated mercury vapour which they inhale when the retorts are emptied.

Some of the difficulties of treating cinnabar by the roasting process are as follows:—

1. The amount of mercury in the ores is small, sometimes only 0·2 or 0·3 p.c., and part of this is obstinately retained by the residues, necessitating long-continued treatment at a red heat.

2. The mercurial vapours readily penetrate the brickwork of the furnace and condensers. This is checked by keeping the pressure of the gases inside the furnace and condensers slightly below the outside atmospheric pressure by means of a fan placed at the outlet. By this device also the workmen are protected from the mercury vapours. The exhaust must not be excessive or the retention of the mercury in the condensers would not be complete. The furnaces are now always covered with iron plates, so that penetration of the masonry by mercury occasions only a temporary loss.

3. Liquid mercury penetrates the furnace bottoms. According to Spirek, over 1000 centners of mercury have been recovered from the foundations of furnaces at Idria. To prevent ultimate loss, furnaces stand on iron plates with upturned edges, draining to a little sump where the mercury may collect.

4. The gases from the furnace are acid, owing to the presence in them of SO_2 and SO_3. The condensed water accordingly attacks iron condensers, whilst most other metals, such as copper, would form amalgams with the condensed mercury. Stoneware, glass, and wood, as well as iron are used in the construction of condensers.

5. *Stupp* or mercurial soot is formed, consisting of finely divided mercury together with mercury sulphate, and chloride, and sooty products of the fuel and the bituminous and other constituents of the ore. The soot accumulates in the condensers and is treated subsequently by special processes. At Monte Amiata, it contains 70 or 80 p.c. of all the mercury recovered. Although inconvenient if formed in very large quantities, however, soot is useful when amounting to about 1 p.c. of the ore treated, as it assists the condensed mercury (*quicksilver-mist* or *quicksilver-foam*) to settle in the condensers and dust chambers and reduces the vapour loss by forming a dry crust over the liquid quicksilver.

According to Christy (Trans. Amer. Inst. Ming. Eng. 1884, 13, 547; 1885, 14, 206), the issuing gases are saturated with mercury vapour at New Almaden, and the loss as vapour can be calculated from the vapour pressure of mercury at the temperature of the gases. According to Spirek, however (Min. Ind. for 1897, 6, 571), the gases at Monte Amiata had a saturation of only 30-45 p.c., owing to the action of the stupp. In any case, it is clear that the temperature and volume of the issuing gases should be kept as low as possible.

The mist loss, due to fine particles of mercury being carried away mechanically in the effluent gases, depends on the method of condensation and the velocity of the gaseous current. It is usually from 2-2½ times the vapour loss.

According to Duschak and Schuette (Ming. and Sci. Press, Sept. 7, 1918, 315; Technical Paper No. 209, U.S. Bureau of Mines) the losses in the stack-gas at two mines in California were as follows in grammes of mercury per cubic metre of gas:—

	New Idria		
	Old plant	New plant	Oceanic
Total loss . .	0·029	0·085	0·047
Vapour loss . .	—	0·052	0·034
Mist loss (by diff.) .	—	0·033	0·013

The total losses in the issuing gases were about 1 p.c. of the mercury in the ore at the new condensing plant at New Idria and 1·3 p.c. at the Oceanic. The gas leaving the old condenser system at New Idria was only half saturated with mercury vapour. The loss in the effluent condenser water was about one-third of the loss in the gases at New Idria but was negligible at the Oceanic. The loss due to absorption of mercury by porous materials used in the construction of the condenser system may be much greater than the fume loss.

The total losses of mercury, which, according to Schnabel, formerly amounted to 50 p.c. or more, have now been reduced to 5 p.c. or even less of the mercury present in the ores, in spite of the great fall in the richness of the ores treated. This reduction of loss is partly due to the labours of the metallurgists at Idria since 1870, the names of Exeli, Langer, Czermak, Spirek, Novak, and others being associated with improvements in the methods of treatment. Much progress is also due to the work of the Italians at Monte Amiata, and especially of the Americans (Scott and others) in California.

Ores are not usually finely crushed for the roasting process, and they are seldom prepared for reduction by means of concentration in water. For ten years the ore at the Cornacchino mine, Monte Amiata, was dressed, with the production of a concentrate containing 25 or 30 p.c. of mercury, and tailing assaying from 0·6–1 p.c. of mercury which was thrown on the dump. The tailing was subsequently treated at a profit in the continuous fine ore roasters and concentration has been discarded (Mineral Industry for 1897, 6, 569).

In 1914, however, several concentrating plants were at work in California on ores which were too poor for treatment in furnaces without being dressed previously. W. W. Bradley has shown on an experimental scale (Quicksilver Resources of California, 1917) that certain friable ores with crystalline cinnabar give high recoveries with water concentration on tables. Slimed cinnabar is lost but can be recovered by flotation, using a mixture of turpentine and petroleum. A combination of the two methods of concentration is therefore indicated. Bradley also found that mercury ores could be treated by leaching with alkaline sulphide (Na_2S and NaOH). These methods have not yet passed the experimental stage.

Types of furnaces. A number of different furnaces have been used for the treatment of mercury ore in the course of the last 100 years. In the discontinuous shaft furnace (Aludel and Idria furnaces) the ore in the form of lumps, or fines made into balls, was piled in a shaft on a perforated arch or grate and heated by the products of combustion of a fire placed below. Shaft furnaces working continuously (Exeli, Langer, and Knox furnaces) succeeded, in which there was no grate to support the ore. The heating gases entered the shaft at the side some distance from the bottom. In a more recent type of continuous shaft furnace for treating coarse ore (Hähner, Valalta, Novak, and Spirek furnaces) there is no external fire, the ore being charged in mixed with charcoal.

In fine-ore shelf furnaces (Huttner and Scott, Livermore, Czermak, and Czermak-Spirek furnaces) the ore passes down over a series of sloping shelves and is heated by the gases from an external fire. These furnaces are more economical than the coarse-ore furnaces and are in wider use. Reverberatory furnaces (Alberti, Exeli ironclad reverberatory, Czermak-Spirek reverberatory) are used in certain cases. Lastly there are the retort furnaces.

A more detailed description of some of these furnaces is appended.

Aludel or Bustamente furnace.—This old-fashioned form of furnace was still in use at Almaden in 1907 and is probably not yet entirely discarded. It is an intermittent shaft furnace, designed by Barba in Peru and introduced into Almaden by Bustamente in 1646. One form of Aludel furnace using wood as fuel is shown in elevation and plan in Figs. 1 and 2, and another and later form with a grate for coal is Figs. 3 and 4. In Fig. 1, *a* is the fire-door, *b* the fire-place, c a perforated brick arch above which is the circular distillation chamber, 4 feet 3 inches in diameter in the smaller furnaces, and 6 feet 6 inches in the larger. The ores are first charged in through the opening *d*, which is afterwards bricked up and charging is completed through the door in the top arch. The total height of the cylindrical shaft is from 20–26 feet. On the arch *c* is placed 2000 kilos. of quartz or of poor ore in large pieces, so that the flames rise through them readily. This is covered with 10–14 tons of ore, beginning with ore of medium quality (*requiebro*, containing from 7–15 p.c. of mercury). Upon this is charged the poorer ores (*china*, containing about 1 p.c. of mercury), then the rich ore (*metal* containing over 15 p.c. of mercury), and lastly small ore of mixed quality (*vasisco*) made into balls.

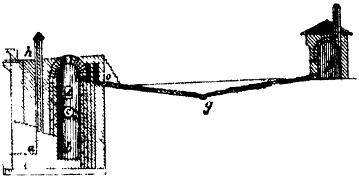


FIG. 1.

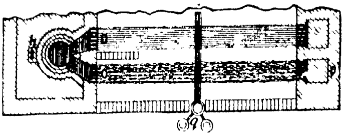


FIG. 2.

The furnace is then closed and the charging doors luted up, and the aludels are luted together in position. These are pear-shaped clay condensers, 18 inches long, glazed on the outside, and so shaped that the narrow end of each fits into the wider end of the next following one. They are arranged in 12 parallel rows each containing 40–45 aludels, lying in grooves on a sloping roof, *ff′*, Figs. 3 and 4. The aludels communicate with condensing chambers *k*, Figs. 3 and 4, *p*, Fig. 1. The products of combustion from the fire pass in part through the flue *h*, Fig. 1, *e*, Fig. 3, but mainly through the

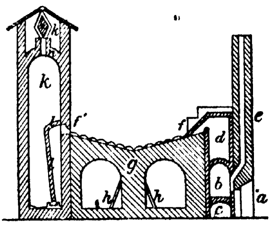


FIG. 3.

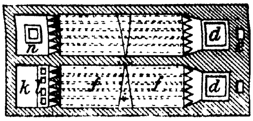


FIG. 4.

bed of ore. The mercurial vapours, sulphur dioxide, and the products of combustion of the fuel pass through the aludels where partial condensation takes place and into the chamber *k*, Figs. 3 and 4, passing below the partition *l*. The condensed mercury in part drains out of the aludels into cast-iron pans situated below (*q*, Fig. 2). In the coal furnace shown in Fig. 3, the mercury drains from the aludels at *g*, through the wooden pipes, *h*, to cisterns filled with water.

The fire is maintained for 10 or 12 hours, thus heating the column of ore sufficiently to enable the cinnabar, pyrites, and bituminous matter to burn in the current of air, which is raised to a temperature of 200°-300° by passing through the layer of quartz before it reaches the ore. The ores burn for 44 hours, a period during which the first aludel reaches a temperature of 245°-260°, and the last aludel one of 29° somewhat later (Kuss, Ann. des Mines, 1877, 13, 39; 1878, 15, 524). The furnace is then opened and the residues allowed to cool for 18 hours, after which they are withdrawn and the furnace recharged.

The aludels are cleaned out once in one or two months, according to position, and the soot collected and prepared for re-treatment. The losses of mercury, according to Langer (Berg. u. Hüttnm. Jahrb. Berg-Akad. 1879) amounted in 1879 to an average of 20 p.c. (*See* also Moreau, Le Génie Civil, 1884, 380; Eng. and Ming. Jour. 1881, 32, 335.)

Idrian furnace.—The aludel furnaces were introduced at Idria about 1750, but were soon altered into the form known as Idrian furnaces, in which the condensing apparatus consists of large brick chambers in place of aludels. These furnaces gave higher percentage losses than aludel furnaces but were worked more cheaply. They were discarded at Idria in 1870. (*See* Schnabel and Louis, *l.c.* ii. 352.) For description of older methods of ore treatment at Idria, *see* Mitter (Vortrag auf dem Bergmannstag zu Klagenfurt, 1893); also Agricola (De re Metallica, Lib. ix. 1556).

Exeli furnace.—The introduction of shaft furnaces fired continuously marked a great advance on the older forms. One of the earliest of these was the Exeli furnace, built at Idria in 1872 (Das K. K. Quecksilber bergwerk Idria in Krain, Vienna, 1881; Schnabel and Louis, *l.c.* 358), and introduced by Randol at New Almaden in 1874 (Egleston, *l.c.* ii. 857). It was surrounded by three external fireplaces and cased in wrought iron to prevent loss of mercury. It was afterwards altered by bricking up the fireplaces and charging charcoal with the ore at the top of the furnace. For the *Langer furnace*, *see* Schnabel and Louis, *l.c.* ii 365, and for the *Knox furnace*, *see* Egleston, *l.c.* ii. 841.

Novak furnace.—This is a good example of a continuously working shaft furnace in which the ore and fuel come into direct contact. It is suitable for coarse ore in cases where charcoal can be obtained cheaply. The earliest shaft furnace of the kind was the Hähner furnace, used at Idria from 1849 to 1852 (Schnabel and Louis, *l.c.* ii. 407). It was replaced by the Valalta furnace (Berg. u. Hüttmn., Ztg. 1864, 284; 1868, 32; Eng. and Mng. Jour. 1872, 14, Nos. 11 and 12). The Novak furnace was introduced at Idria in 1892. One of these furnaces is shown in elevation and plan in Figs. 5 and 6, but three furnaces are united in a single block. The outer walls are cased in iron plates. The shaft *a* is rectangular, 7 metres in height and 2 metres by 2·4 metres in cross section at its widest part. There are four openings, *b*, *b*, for the removal of the residues. The brick shaft stands on a cast-iron plate, *c*, supported by legs and standing on a brick foundation, accessible also from below at *d*. Any loss of mercury in the foundations is thus prevented. The roof-shaped ridge *e*, in the bottom of the furnace, is pierced with many small holes for the supply of air. The charging hopper *f* is fitted with a water-joint and the pipe *g* leads to the condensers. Poor ore in lumps not smaller than 0·67 inch mesh and pressed soot are treated, one ton of ore together with 16 p.c. of its weight of charcoal being charged into the furnace every 2 hours. The condensers are of the usual Czermak type, *see* Fig. 11. The production of soot amounts to 0·5 p.c and the loss of mercury to 7 or 8 p.c. With furnaces of this type the formation of soot is much less than in the fine ore furnaces about to be described.

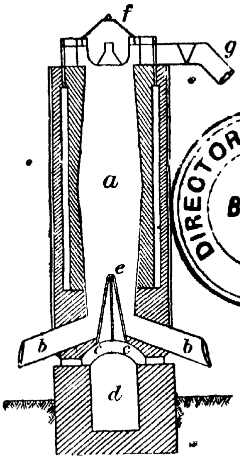


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FIG. 5.

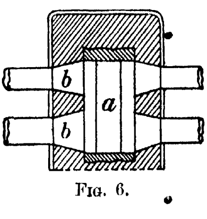

FIG. 6.

The modern Czermak-Spirek shaft furnaces used at Siele, Monte Amiata, in which the loss is only 2 or 3 p.c. of mercury, are described in the Mineral Industry for 1901, 10, 559. (*See* also Spirek, Sixth Internat. Cong. of Appl. Chem. Rome, 1906.)

Hüttner and Scott furnace (Schnabel and Louis, *l.c.* ii. 372; Egleston, *l.c.* ii. 864). This furnace was introduced at the New Almaden mines, California, in 1875, and was the earliest of the shelf furnaces, which are especially suitable for treating fine ore. At New Almaden the small ore of less than 1·2 inch cube was called *tierras*, and the larger ore of between 1·2 inch and 2·3 inch cube, was known as *granzitas*. These materials were treated in separate furnaces built on the same principle, with a large number of inclined shelves sloping at an angle of 45° in alternately opposite directions, upon which the fine ore slides down, filling up the spaces between the shelves. The products of combustion of the fire pass horizontally between the under side of the shelves on each tier and the surface of the ore resting on the shelves of the next tier below. The ore is thus heated and roasted, and is finally discharged at the bottom of the furnace.

One of the newer forms of this furnace was built by Newcomb at Oat Hill, California, in 1898 (Mineral Industry, 7, 583). Fig. 7 is a vertical section through the furnace and the first section of the condensers; and Fig. 8 is a front view, with the furnace in section and the condensers partly in elevation. Fig. 9 is a horizontal section of the furnace on A, B, Fig. 8.

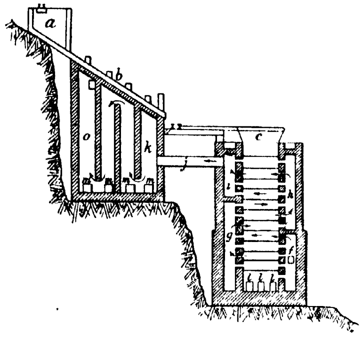

Fig. 7.

The ore is passed through 1·5 inch gratings before entering the ore-bin *a*, Figs. 7 and 8, whence it passes over a drying platform *b*, placed above the condenser, and is discharged into a hopper, *c*. The hopper is kept full of ore which acts as a seal when a slot is opened and some ore let fall into the furnace. Two tons of ore are thus charged in at intervals of one hour.

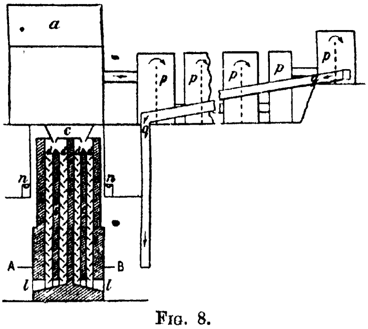

Fig. 8.

The furnace is of brick, 22 feet by 16 feet, and 37 feet high, outside measurements. The roasting chamber is divided into four compartments, *d*, Figs. 8 and 9, by three vertical partitions, *e*, and in each compartment is a series of 24 sloping shelves (*see* Fig. 8) consisting of fire clay tiles, which allow the ore to slide down in a zig-zag path. The ore piles up on the shelves bridging over the 6-inch spaces between them, so that the products of combustion from the fire-box, *f*, Figs. 7 and 9, cannot rise vertically in the shaft but pass horizontally under the shelves from *f* to *g*, thence from *g* to *h*, following the course indicated by the arrows, and finally from *h* to *i*, whence they escape by two cast iron exit pipes *j*, to the condenser *k*.

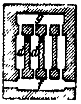

Fig. 9.

The spent ore is discharged by being raked, at intervals of 15 minutes, through the openings *l*, *l*, which are placed 5 feet below the level of the fire-grate, so as to enable the ore to be cooled before it is withdrawn. The furnace holds 40 tons of ore, so that the ore remains under treatment about 20 hours. The fuel used is 2½ cords of wood in 24 hours. The temperature is kept as low as possible, a cherry-red heat being aimed at, and hardly a trace of cinnabar is found in the material discharged.

The condensers are of brick, with cemented floors sloping down to the discharge apertures *m*, *m*, Fig. 7, whence the metal runs to the quicksilver troughs *n*, *n*, Fig. 8. Very little mercury is condensed in the first compartment *k*, but the amount increases up to the last compartment *o* of the first condenser. After this, in passing through the remaining six brick condensers *p*, *p*, Fig. 8, the amount of mercury recovered decreases. The fumes next pass into the wooden flue condenser *q*, Fig. 8, eventually being discharged into the open air through a vertical flue in which an exhaust fan is placed. The length of travel in the condensers is 400 feet. About 30 p.c. of the total yield of mercury is obtained from the soot. The loss of mercury is estimated at about 5 p.c., and the labour required is 4 men per shift with a fifth during the day to attend to the soot-pan.

In California, the Scott furnaces are in general use, the ore being only crushed to 2 or 2¼ inches diameter, so that the fine-grinding evil is avoided. Shaft furnaces appear to have been discarded in California, as less advantageous than the shelf furnaces.

Multiple-hearth mechanically-stirred furnaces have also been in use in California, and it is claimed that they are less costly to build and operate. However, they require more skilled labour and more frequent repairs involving delay, and have fallen into disuse. Rotary furnaces of the cement-kiln type were introduced at the New Idria Mine in 1918 and proved highly successful. Wet ores could be treated without being dried, but ores containing a large amount of sulphur or an excessive amount of fines were less amenable in the rotary furnace, and are considered more suitable to the Scott furnaces (Eng. and Mng. Jour. 1919, 107, 86).

Czermak-Spirek continuous roasting furnace

(Mineral Industry for 1897, 6, 572). This furnace is a modification of the Czermak furnace introduced at Idria in 1886 (*see* Schnabel and Louis, *l.c.* ii. 388). It is on the same principle as the Scott furnace, and is similar in being suitable for the treatment of fine ore.

It consists of a rectangular chamber of iron, with two fireplaces, one at each end. The fires are lighted alternately, only one being at work at any given time. The products of combustion pass into a wide flue or combustion chamber extending longitudinally in the middle line of the furnace near its base. Hot air from iron pipes used to cool the ore just before it is discharged is used for combustion, and an excess of air is supplied.

The ore is fed from above upon **V**-shaped tiles, with the apex upward, ranged in parallel lines, in such a way that the apex of each tile is opposite the space between two tiles in the layer next above (*see* Fig. 10). The ore slips down the tiles and completely fills the space *a* between two successive layers of tiles. When part of the residues are withdrawn from the bottom of the furnace, there is a general subsidence of ore extending to the top. There is a regular system of oval openings in the sides of the furnace provided with movable covers, through which iron bars may be introduced to dislodge the sintered ore in case of necessity. The **V**-shaped tiles are supported on longitudinal walls made of perforated bricks.

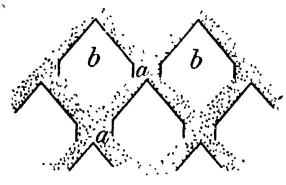

FIG. 10.

The products of combustion and hot air from the combustion chamber circulate through the furnace by the passages *b*, between the tiles and the ore and pass out at the top of the furnace through cast-iron pipes into the condensers. The temperatures in the furnace are as follows: ore on discharge, 100°; air supplied for combustion, after being used to cool the roasted ore before it is discharged, 300°-360°; combustion chamber, 800°-900°; in the first tier of tiles of the roasting zone, 700°-800°; in the fourth and highest tier, 360°-400°; in the passage to the condenser, 260°-360°.

The condensers are of the usual Czermak pattern, consisting of cast-iron pipes of elliptical section (*a*, Fig. 11). In positions where the temperature is below 100° so that the acid vapours are condensed, the iron is lined with cement to avoid corrosion of the iron. Glazed stoneware is also used instead of cast iron. These condensers are cooled with water. The lower part *b* of the condensers is sometimes constructed of wood, and dips for about two inches into water contained in lined cast-iron or wooden boxes, *c*. The flue leading from the furnace is shown at *d*. The vapours escape into the wooden flue *e*. The large furnaces have two sets of condensers which can be cleaned alternately without stopping the work of the furnace. From the condensers, the vapours pass into flat wooden flues, or dust chambers, in which a poor soot is collected.

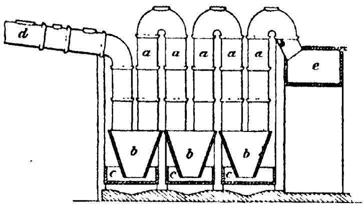

FIG. 11.

The pressure of the vapours within the furnace and condensers is kept below atmospheric pressure by means of a fan which provides an exhaust equivalent, according to Spirek, to a water column of about 4 mm. at the outlet or 1 mm. at the junction between the furnace and the condensers.

The capacity of the furnace depends on the nature of the ore, and in the case of the largest sized furnace at Siele varies from 16-26 tons per day. The ore remains in the furnace from 41-68 hours, and is shifted by the withdrawal of a portion every 2 or 3 hours. The ore is roasted at a bright red heat until the last trace of mercury has been driven off. The condensation is also very good, about 90 p.c. of the mercury and soot collecting in the first 3 **U**-tubes, within a length of 4 metres. The greater part of the metal, and in the case of low-grade ores the whole of it, remains in the soot, and is recovered in part in soot presses, or by rubbing on an inclined surface and in part by redistilling the soot in a small continuous roaster of the same pattern. At Monte Amiata, the average loss of mercury with these roasters is 4 or 5 p.c., after the impregnation of the wooden condensers is completed. Two workmen per shift are sufficient to attend to this furnace, one on the charging floor, the other as fireman.

These furnaces are in use at Monte Amiata, Idria, Almaden, and elsewhere.

Reverberatory furnaces are used for the treatment of fine ore which yields too much flue dust when treated in shelf furnaces, and also for coarse ore which decrepitates or sinters readily.

The first reverberatory was employed by Alberti at Idria in 1842, and the latest form is the Czermak-Spirek long-bedded calciner introduced in 1888 and shown in Figs. 12 and 13.

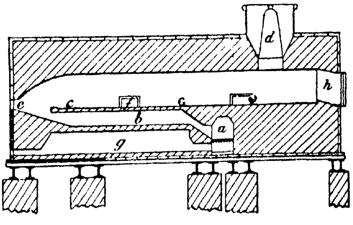

FIG. 12.

Two furnaces are placed side by side in one block and stand on a dish of riveted sheet-iron. The fire-grate *a* extends across almost the whole width of the furnace. The flame traverses the flue *b* under the bed of the hearth and then passes over the tiled hearth *c*, which is 5½ metres long and 2·4 metres wide. The charging hopper is at *d*, and there are five working doors at *e* and *f*. The residues are withdrawn every 2½ hours through the door *f* into the receptacle *g*. The gases and vapours pass through the openings *h* into Czermak condensers of the usual pattern.

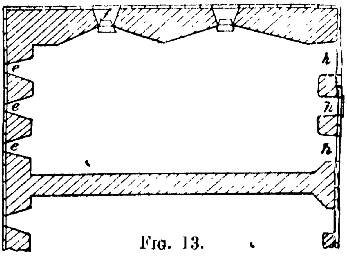

FIG. 13.

These furnaces treat 6·6 tons of poor ore and soot in 24 hours with a consumption of 148 cubic feet of wood per 10 tons of ore. The production of soot amounts to 1·9 p.c. and the loss of mercury to 8 or 9 p.c (Schnabel and Louis, *l.c.* ii. 402).

For the description of a similar reverberatory furnace designed by Spirek for the treatment of mercury-lead ores, *see* Mineral Industry for 1902, 11, 548.

Retort furnaces were used for a time at Idria, Monte Amiata, and California, but are probably no longer in use in any part of the world except, according to Schnabel, at Littai, in Carniola. The ore is mixed with lime or iron and heated in cast-iron or clay retorts, which are pear-shaped or cylindrical in shape, and usually contain from 1–5 cwt. of ore. The method is suitable only for rich ore or soot, but even for such material the process gives no better results than the air-roasting process, and apart from cost, it has the disadvantage of producing concentrated vapours of mercury which have injurious effects on the workmen.

At Littai (Schnabel and Louis, *l.c.* ii. 421), cast-iron retorts are used, taking a charge of 2 cwt. of ore. The ore contains 2 or 3 p.c. of mercury, and 5 or 6 p.c. of lime is added. The retorting lasts 6 hours and the loss of mercury is stated to amount to from 5–6 p.c.

Soot or *Stupp*, the deposit on the walls of the condensers, consists of finely divided mercury and compounds of mercury, together with carbon, tarry matters, and ash from the fuel and dust from the ore, amounting in all, according to Spirek, to about 1 p.c. of the ore at Monte Amiata. The composition of soot varies largely. One sample from the condenser of a Czermak furnace was found to contain :

Metallic mercury	22·01 p.c.
Mercury as cinnabar . . .	6·75 ,,
Mercury as sulphates, chlorides, &c.	3·04 ,,
Total mercury . .	31·80 ,,

(*See* Schnabel and Louis, *l.c.* ii. 425, where many analyses are given.)

The soot is usually treated mechanically to separate part of the mercury contained in it. It may be worked with hoes on an inclined surface until no more mercury flows off, as at Almaden (Berg u. Huttnm. Jahrb. der K. K. Montanlehranstalten, 27, 46). When rubbed with lime, more mercury is separated.

At Idria and Monte Amiata, Exeli stupp presses are used. These are iron pans fitted with vertical knives fastened to the bottom. Revolving arms carrying similar knives stir the soot and press it against the stationary knives. Lime is added little by little to the extent of from 17–30 p.c. of the soot during the course of the operation, which occupies one or two hours in the case of rich material. When the soot is stirred and pressed, mercury separates from it and flows away through small openings in the bottom of the pan.

The soot residues after treatment still contain 10 p.c. or more of mercury and are treated mixed with ore in the same furnace as before, or mixed with other rich materials in similar furnaces of small size, or more rarely in retorts. Formerly where coarse ore furnaces were in use, the soot residues were moulded into bricks and treated with the ores.

Purification. Impure mercury is recognised by the fact that globules are pear-shaped with tails, instead of spherical, when made to run down a sloping surface, and may even leave a trail behind them on paper. Mechanical impurities are removed by squeezing through chamois leather or by filtering through punctured blotting paper.

Retorting at a low temperature with a cover of charcoal and lime will remove most of the impurities. Oxidisable impurities are best removed by the passage of a stream of air through the mercury, which is covered with dilute nitric or sulphuric acid. The base metals are rapidly oxidised by the air and dissolved by the acid (*cf.* Harries, Zeitsch. angew. Chem. 1921, 34, 359). Small quantities of impurities may be removed merely by digesting or shaking mercury with dilute nitric acid.

Mercury is kept in a glass or stoneware vessel under a layer of dilute nitric acid of sp.gr 1·1 and drawn off as required by a stopcock at the bottom and washed with water before use.

Properties. Mercury is a silver-white liquid metal with a slight bluish tinge. In thin films it transmits violet light (Melsens). Its sp.gr. at 0° is 13·59545 when compared with water at 4° (Volkmann, Thiesen and Scheel). At −38·85°, (Balfour Stewart), −38·87° (Wilhelm), −38·89° (Henning), it solidifies, contracting considerably and forming a tin-white, soft, malleable and ductile metal of sp.gr. 14·193 at its melting-point (Mallet, Phil. Mag. 1877, [v.] 4, 145). Its density in the liquid state at the same temperature is 13·690 (Vicentini and Omodei). Its electric conductivity is $1·063 \times 10^4$ at 0° (Dewar and Fleming); and its thermal conductivity K at 0° is 0·0148 (H. F. Weber). For thermal expansion *v.* Callendar and Moss, Phil. Trans 1911, 211 A, 1; Chappius, Bureau Int. Poids et Mes. Mem. 1917, 16.

It is volatile at ordinary temperatures and even at −44° (Merget); its b.p. is 357·25° at

760 mm. pressure (Regnault), 356·7° (Heycock and Lamplough), forming a colourless vapour. (For its vapour pressures from 40°–512°, *see* Ramsay and Young, Chem. Soc. Trans. 1886, 49, 37.) According to Brönsted and Hevesy a partial separation of isotopes of mercury may be made by evaporating the metal at low pressures and condensing the evaporated atoms on a cooled surface. The density difference found between the heaviest and lightest mercury amounts to 0·49 p.c., corresponding with a difference of 0·1 unit in the atomic weight (Zeitsch. physikal. Chem. 1921, 99, 189). Its critical temperature is 1172° (abs.), and pressure 180 atm. (van Laar); 1077° and 420 atm. (Ariès, Compt. rend. 1918, 166, 334), 1723° (abs.), and 1042 atm. (Weber).

It is unaltered in air, oxygen, nitrous and nitric oxides, carbon dioxide, &c., at ordinary temperatures. When heated to about 350°, it becomes gradually converted into the red oxide, HgO, which is decomposed below a red heat.

Mercury is not acted on by HCl, and is almost unaffected by dilute H_2SO_4, although dissolved by hot strong H_2SO_4. It is dissolved even by cold dilute HNO_3, and is rapidly attacked by hot or concentrated nitric acid. It is also dissolved by aqua regia.

Neutral and acid solutions of ferric chloride are reduced when shaken with mercury Under similar conditions titanic acid is not reduced. Solutions of potassium ferricyanide, chromate, ammonium molybdate, sodium vanadate, and potassium antimonate when acidified with hydrochloric acid are reduced on shaking with mercury.

When agitated with oils, turpentine, &c., or triturated with grease, fats, sulphur, certain sulphides, arsenides, &c., mercury is subdivided into minute globules, not easily reunited. This is known as the flouring, sickening, or deadening of mercury and is the cause of losses in the extraction of silver and gold from their ores by amalgamation. The coalescence of floured mercury can be effected with some loss by the action of nitric acid.

Vapours of mercury have a poisonous effect ('salivation') on the animal system. Among the remedies are cleanliness, fresh air, acid foods, and moderation in the use of alcohol. The use of potassium iodide is also recommended.

Uses. Mercury is used in the extraction of gold and silver from their ores, for the manufacture of vermilion (*v. infra*), and of fulminates, in medicine, in dentistry, and in the manufacture of barometers, thermometers, and of other scientific apparatus. The metal and its amalgams are used in small quantities for a variety of other purposes.

The consumption of mercury in silver-milling was formerly very large when the pan amalgamation process was in wide use. In treating the ores of the Comstock lode, for example, 7 lbs. of mercury was formerly lost in the treatment of a ton of ore. In modern stamp-battery practice on gold ores, the loss is only 0·2 or 0·3 oz. of mercury per ton of ore. The development of the cyanide process and the abandonment of the patio and pan amalgamation processes have caused a reduction in the amount of mercury required in the extraction of silver ores. Its consumption in the manufacture of fulminates was very great during the war, and paint for ships' bottoms is also stated to consume large and increasing amounts.

The *production* of mercury during the years 1918–1920 in tons was as follows (*see* Quicksilver, 1913–1919, Imperial Mineral Resources Bureau, 1922):—

—	1918	1919	1920
Austria . .	413	[1]	[1]
Hungary . .	83	—	—
Italy . . .	1021	831	1303
Mexico . .	161	117	75
Spain . .	558	1207	848
United States .	1101	717	438
China (exports) .	289	79	45
Total .	3626	2951	2709

Mercury is transported in wrought-iron flasks or bottles closed by screw stoppers. The weight of mercury in a Spanish flask is 34·507 kg. or 76 lbs. It was formerly 76·5 lbs. but in California was reduced to 75 lbs. in 1904. In England the price is quoted per flask of 75 lb. The old sheepskin bag used to contain 55 lbs.

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Mercury sols can be prepared by various methods—mechanical, thermal, and electrical. When mercury is forced in a fine stream into solutions of gelatin and potassium nitrate, definite mercury sols are produced, or when mercury is shaken with very dilute solutions ($10^{-5}N$) of ammonia, ammonium sulphate, ammonium chloride, calcium citrate, tartaric acid, potassium tartrate or gelatin, or by passing hot mercury vapour directly into water. They have varying colours, from grey to yellowish-brown and reddish-brown (Nordhund, Diss. Upsala, 1918, 1).

COMPOUNDS OF MERCURY.

Mercury forms two series of salts: the *mercuric* compounds, in which the metal is divalent, and the *mercurous* compounds, in which it is apparently monovalent.

The *mercuric salts* are often obtained when excess of acid acts on metallic mercury. Reducing agents convert them into mercurous salts, which may be further reduced to metallic mercury. The soluble salts are extremely poisonous and are acid to litmus.

The *mercurous salts* are produced when an acid acts on excess of mercury, or by the reduction of mercuric compounds. In solution they readily dissociate into metallic mercury and a mercuric salt (Hada, Chem. Soc. Trans. 1896, 1667). This reaction is reversible and ends with the establishment of equilibrium between the mercurous and mercuric ions present (Abel, Zeitsch. anorg. Chem. 1891, 26, 361).

Mercury forms three oxides, *mercurous oxide, mercuric oxide*, and *mercuric peroxide*.

Mercurous oxide Hg_2O is obtained as a blackish-brown powder by the addition of alkalis to a solution of mercurous salt, or by triturating a solution of alkali with calomel. It is washed, dried spontaneously, and kept in the dark. By the action of light or of a gentle heat it is decomposed into the red oxide and mercury, and it combines with oxygen at 100° (Colson, Compt. rend. 1899, 128, 1104). It may be obtained in colloidal solution by treating the aqueous solution of mercurous salt with alkali salts of the albinic acids in presence of alkali hydroxide or carbonate (Hofmann, D. R. P. 185599, 1905; J. Soc. Chem. Ind. 1907, 1254).

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[1] The production of Austria is included in that of Italy in 1919 and 1920, as Idria is now in Italian territory.

Mercurous hydroxide does not exist at the ordinary temperature, but is obtained as a bright yellow precipitate by the action of alcoholic potash on alcoholic mercurous nitrate at −42° (Bird, Amer. Chem. J. 8, 826).

Mercuric oxide, *Red oxide of mercury, Red precipitate*, HgO. This oxide is slowly produced when the metal is heated in air to near the boiling-point. It may be obtained pure by pouring a boiling solution of mercuric chloride into an excess of boiling potassium carbonate solution and boiling till the precipitate is of the right colour (Dufau, J. Pharm. Chim. 1902, 16, 439). It is usually prepared by heating the nitrate until nitrous fumes cease to be evolved, but not sufficiently to decompose the oxide itself. When prepared slowly on the large scale the oxide is obtained in fine brick-red crystalline plates of sp.gr. 11·163 (Playfair and Joule).

By precipitating a mercuric salt with cold potash, the oxide is obtained as an orange-yellow powder of the same composition, but more easily acted on by reagents. With oxalic acid it produces the oxalate, whilst the crystalline oxide is not so affected. When heated with mercuric chloride solution it rapidly forms an oxychloride; the crystalline form is only slowly so converted. The amorphous oxide is also more easily decomposed by heat. It was formerly considered by many chemists that the red and yellow oxides differed only in the size of the particles (*see e.g.* Ostwald, Zeitsch. physikal. Chem. 1900, 34, 495; Schick, *ibid.* 1902, 42, 155). Schoch, however, has shown (Amer. Chem. J. 29, 319) that the crystalline form of the red is different from that of the yellow oxide, that the dissociation pressure of the yellow oxide at 300° is considerably greater than that of the red oxide, and that when heated at 250° it is converted into the red oxide with partial decomposition.

Mercuric oxide is a powerful poison. It dissolves in about 20,000 parts of water at 25° or about 2200 parts at 100° (Schick, *l.c.*). It is slightly soluble in solutions of sodium hydroxide (Fuseya, J. Amer. Chem. Soc. 1920, 42, 368). When heated it becomes bright red, and finally nearly black, but regains its colour on cooling. A superficial change of colour from bright red to brownish-red is produced when the red oxide is exposed to light. When strongly heated, it is decomposed into mercury and oxygen. By this reaction, oxygen was first prepared by Priestley.

When heated with zinc, tin, or antimony filings, the oxide is reduced to metal with incandescence. When added to fused sodium the action is still more intense. The mixture with sulphur explodes violently when heated. Mixed with phosphorus it detonates when struck. At a red heat it is converted by chlorine into mercuric chloride, with liberation of oxygen. It dissolves in fused potash with formation of a double oxide, without evolution of gas.

Mercuric oxide is frequently used as an oxidising agent in chemical operations.

A colloidal solution of mercuric oxide is obtained when mercuric chloride solution is treated with the sodium salts of protalbinic or lysalbinic acids and caustic soda. A yellow solution is obtained which can be purified by dialysis and then gives on evaporation *in vacuô* at 40° red-brown plates of the stable hydrosol (Paal, Ber. 1902, 35, 2219).

Mercury peroxide HgO_2 is formed in small quantities during the catalytic decomposition of hydrogen peroxide by metallic mercury (Antropoff, Zeitsch. Elektrochem. 1906, 12, 585), and is prepared by the interaction of alcoholic mercuric chloride, hydrogen peroxide, and alcoholic potash (Pellini, Atti. R. Accad. Lincei, 1907, [v.] 16, ii. 408). Either method yields the anhydrous peroxide as an amorphous, brick-red powder, which is fairly stable in dry air. It is slowly decomposed by water, and with acids yields a mercuric salt and hydrogen peroxide: with hydrochloric acid chlorine is liberated.

Mercuric sulphide HgS occurs native as *cinnabar*, which is the principal source of the mercury of commerce. Cinnabar is found, granular or massive, in sub-transparent rhombohedral crystals which cause circular polarisation of transmitted light. It has a cochineal-red colour and gives a scarlet streak.

Mercuric sulphide exists in three different crystalline forms: (1) cinnabar δ-HgS, sp.gr. 8·176, readily prepared by digesting any form of mercuric sulphide with a solution of alkali sulphide; (2) metacinnabarite (black and cubic) α'-HgS, sp.gr 7·60, precipitated from dilute acid solutions of mercuric salts by sodium thiosulphate; and (3) β'-HgS, sp.gr. 7·20, obtained as a fine crystalline powder from more concentrated neutral solutions of mercuric salts with sodium thiosulphate. Cinnabar is the stable form of mercuric sulphide at all temperatures up to its sublimation point, about 580° (Allen and Crenshaw, Amer. J. Sci. 1912, [iv.] 34, 341). Mercuric sulphide fuses at 1450° in an atmosphere of nitrogen under 120 atm. pressure, forming a matt steel-grey solid which becomes red when rubbed (Tiede and Schleede, Ber. 1920, 53, 1717).

The black sulphide is produced by the action of hydrogen sulphide on solutions of mercuric salts, or by triturating or heating mercury with sulphur. Thus prepared it was formerly used in medicine under the name of *Æthiops mineral.* It occurs native in California (Moore, J. pr. Chem. 1870, [ii.] 2, 318).

Under the name of *vermilion*, the red variety is prepared on the large scale and used as a pigment. Native cinnabar cannot be so used because of impurities which affect the colour. Vermilion is prepared both by *dry* and *wet* processes.

Dry processes.—These all depend on the preparation of the black sulphide, usually by the combination of mercury and sulphur, and its subsequent conversion into the red variety by a process of sublimation. The following method was formerly largely used in secret in Holland. 1080 lbs. of mercury and 150 lbs. of powdered sifted sulphur are moderately heated in an iron pan with constant stirring, and the black *æthiops* obtained is cooled and powdered. This is introduced in charges of about 25 lbs. four times an hour into long subliming pots of refractory clay, each holding about 410 lbs., heated from below to about two-thirds of their height. As each charge is added it ignites, and a long flame escapes from the pot; when this has subsided, the pot is covered with an iron plate. The operation occupies about 36 hours. The pots are cooled and broken, and the vermilion, which is principally in the upper portions, is ground with water between stones, sifted, elutriated, and dried.

It is said that if 1 part of antimonious sulphide be added to the mixture of sulphur and mercury before sublimation, and the vermilion be digested with potassium sulphide, an improved pigment is obtained which contains no antimony.

At Idria, a mixture of 8 lbs. sulphur and 42 lbs. mercury is placed in a well-bound cask, which is rotated for some hours until the contents consist of a uniform brownish powder.

A number of vertical, cast-iron cylindrical retorts heated to dull redness are charged with the mixture, and immediately covered. When crackling has ceased the covers are replaced by stoneware necks, each connected with a tube and receiver. The fire is then increased to drive the whole of the sulphide from the retort.

When cooled the necks are taken off, and the cake of vermilion removed. That nearest the retort is best, whilst that in the receiver contains free sulphur, and is resublimed with a fresh charge. The cakes are broken, ground with water, boiled with sodium hydroxide solution, washed and dried.

The Chinese vermilion is celebrated for its fine colour, which inclines to carmine. It is said to be prepared as follows:—

About half a bottle (38 lbs.) of mercury and 17½ lbs. of sulphur are mixed in an iron pan, about 25 inches wide and 7 or 8 inches deep, and heated by charcoal. When melted, it is stirred with an iron spatula, and the remainder of the mercury is gradually added. When the metal has disappeared the mass is removed from the fire, cooled by the addition of a little water, rapidly stirred, and coarsely powdered. The reddish or black semicrystalline powder, which contains free mercury and sulphur, is placed in a fixed iron pan, and covered with porcelain tiles 8 inches diameter (many of which are broken), arranged in the shape of a dome. The whole is covered by a pan 4 inches less in diameter than the fixed one, to which it is luted by clay, leaving four holes in the luting for the escape of gases. The charcoal fire is then lighted and kept fiercely burning for 18 hours; blue flames are seen burning round the holes, showing loss of sulphur and of mercury. The fires are then allowed to die out and the pans to cool. Most of the vermilion is found adherent to the porcelain, and is removed. That attached to the iron is inferior, and is made with the other waste into cakes with alum and glue water, dried, and resublimed. The sulphide on the porcelain is blood-red and crystalline. It is powdered and ground with water in a handmill between stones, and washed into a vessel. At the close of a day's work a solution of alum and glue (1 ounce of each to 1 gallon of solution) is well stirred with the powder, and the whole is allowed to stand until morning. The glue tends to lengthen the period of deposition, and to render the stratification into the various qualities more perfect. The alum is said to improve the colour. The liquid is decanted, and the upper portions of the deposit are set aside. The lower parts are reground and treated as before, the grinding being sometimes repeated several times. The fine vermilion is stirred in water and settled, and the water is decanted. The residue is dried in the open air, powdered, sifted through muslin, and packed in papers holding about 1⅓ ounce each (*v.* Chem. News, 1884, 50, 77; J. Soc. Chem. Ind. 1882, 1, 195). It is used for making Chinese red-ink—for painting on porcelain and wood and colouring candles and paper. Most of the numerous temples throughout China are painted red, and everything lucky and pleasant among the Chinese is of vermilion colour (J. Soc. Chem. Ind. 1890, 9, 1047).

Wet processes.—The processes most used depend on the action of alkaline sulphides on the amorphous mercury sulphide. The temperature adopted largely influences the colour.

The action of these sulphides is attributed by Ditte (Compt. rend. 98, 1380) to the alternate production and decomposition of a double sulphide of mercury and alkali. In the case of potassium sulphide the compound $K_2S{\cdot}5HgS$ is first produced, and is decomposed at about 45° (the temperature generally employed), with deposition of the *red crystalline* mercuric sulphide, whilst the liberated alkaline sulphide dissolves a further amount of the more readily attacked amorphous sulphide, and again forms the double sulphide, which is again decomposed as before.

In order to prepare a polysulphide free from hyposulphite (which is said to have an injurious effect on the colour), potassium sulphate is converted into sulphide by ignition with carbon. The mass is extracted with water, and boiled with sulphur out of contact with air.

Of this strong solution 2¼ kilos. is digested and agitated with 1 kilo. sulphur and 5 kilos. mercury at a gentle heat. The mixture gradually becomes heated, and in about 2 hours acquires a greenish-brown colour. After a further period of 2 hours it becomes of a rich brown, and is allowed to cool to 50°, and is maintained at that temperature for 3 or 4 days with frequent agitation. A fine-coloured vermilion gradually settles down; it is washed with potash, then with dilute nitric acid, and finally with water (Firmenich, Dingl. poly. J. 1864, 172, 370).

According to Liebig, a fine vermilion is produced by immersing recently precipitated *white precipitate* in a solution of ammonium polysulphide. The mixture at first produced is black, but when heated to about 45° gradually acquires a fine colour resembling that of Chinese vermilion. It may be digested with potash, and washed to improve the colour.

Hausmann (Ber. 1874, 7, 1746) adds excess of dilute ammonia to a solution of mercuric chloride, and dissolves the precipitated *mercuric* *ammonium chloride* in a slight excess of sodium hyposulphite. On warming to 70° or 80° the vermilion begins to precipitate. The heat is continued until the mass has become pasty, the sulphide is then separated as usual. The above temperature and the presence of the ammonia and ammonium chloride are said to be essential.

One of the best processes is that of Brunner (Pogg. Ann. 1828, 15, 593). A mixture of 100 parts mercury with 38 parts sulphur (flowers) is triturated for some hours, mixed with a solution of 25 parts potash in 150 parts water, and digested at a temperature below 45°, keeping the liquid at constant volume by adding water.

After 2 or 3 hours it becomes brownish, and then gradually brightens. The temperature must be carefully regulated and the volume kept constant, or the precipitate loses its pulverulent character and becomes inferior in colour. At the proper point, usually after about 8 hours, the heating is stopped and the contents are washed as quickly as possible, as the further action of the potash would produce a brown colour. It is lixiviated to separate any black sulphide, and dried.

The method of Gauthier Bouchard is strongly recommended. Concentrated ammonia solution is saturated with sulphuretted hydrogen, and 400 c.c. of the solution is digested in a stone bottle with flowers of sulphur, with production of a solution of ammonium sulphide of sp.gr. 1·034. This is mixed with 200 grams of sulphur and 1000 grams of mercury (as pure as possible), agitated well in a closed vessel for about 7 hours, and finally heated for 3 or 4 hours to 50°. The liquid is decanted and the residue is washed with water, followed by dilute nitric acid and finally by water.

The chief difficulty in all these methods is to free the vermilion from alkaline sulphides and sulphur, the presence of which is detrimental to the colour of the product. Picton and Linder therefore recommend (Eng. Pat. 5120, 1892) that the black sulphide, produced by one of the usual methods, be suspended in water and treated with a stream of hydrogen sulphide gas until it dissolves. This solution is then heated in a closed vessel to 160°–170° for several hours, when a very pure vermilion is deposited.

Vermilion is adulterated with red lead, red ochre, chrome red, red oxide of iron, and frequently with gypsum. These all remain on volatilisation of the vermilion in a glass tube. Dragon's blood, if present, gives a characteristic odour on heating; it also dissolves in alcohol with a red colour. Chinese vermilion usually contains a little glue, which is not, however, an adulteration. Mercuric sulphide is occasionally present in vulcanised caoutchouc (Frank and Jacobsohn, Gummi. Zeit. 1909, 23, 1046).

The sp.gr. of red mercuric sulphide is 8·12; that of the black sulphide is 7·5.

Mercuric sulphide when heated in the air is decomposed with production of the metal and sulphur, which is at once oxidised to sulphur dioxide. With lime, alkaline carbonates, or metals such as iron, copper, and tin, it is reduced with formation of alkaline or metallic sulphide. When heated with litharge both lead and mercury are reduced, the oxygen and sulphur combining, and passing off as sulphur dioxide.

If boiled in water with powdered zinc, metallic mercury is liberated. A similar but slower action occurs with copper.

Concentrated nitric acid has no action except after prolonged heating. It is then converted—especially if freshly precipitated—into a white insoluble compound containing both sulphide and nitrate of mercury. It dissolves easily in *aqua regia* and in cold concentrated hydriodic acid. Barium sulphide readily dissolves it.

The solubility of mercuric sulphide in solutions of alkali sulphides has been investigated by Knox (*v.* Abegg's Handbuch der anorg. Chem. Bd. 2, Abt. 2, s. 633; and Trans. Faraday Soc. 1908, 4, 29). The black sulphide is more soluble than the red sulphide and the amount of each dissolved per mol. of sodium sulphide increases with dilution. The compound Na_2HgS_2 exists in the solution, but when evaporated over sulphuric acid it deposits yellow crystals of the composition

$$2Na_2S,5HgS,3H_2O$$

The solubility of the sulphides in water is very small, K_{25} 0·01 0·02 $\times 10^{-6}$ (Name, Zeitsch. anorg Chem. 1904, 39, 108)

Mercuric sulphide can be obtained in colloidal solution by washing the precipitated sulphide with a solution of hydrogen sulphide (Winssinger, Bull Soc. chim. [ii.] 49, 452; Linder and Picton, Chem. Soc. Trans. 1892, 61, 123; *see* also Picton, *ibid.* 139). By saturating with hydrogen sulphide a solution of 12 grams mercuric cyanide in 100 of water, a deep brown solution is obtained which when dialysed gives an unstable hydrosol. If, however, the hydrocyanic acid is distilled off *in vacuô* an oily stable hydrosol is obtained (Lottermoser, J. pr. Chem. 1907, [ii.] 75, 293).

Mercuric sulphoxychloride $[3(SHgCl),HgO]_2$ a white granular powder obtained by the action of diacetylthiocarbamide, diphenylthiocarbamide, and allylthiocarbimide on aqueous solutions of mercuric chloride (Ray and Sen, Chem. Soc. Trans. 1919, 552).

Mercurous sulphide Hg_2S is not known.

Mercurous chloride, *Calomel* Hg_2Cl_2, occurs native in small quantities as *horn-quicksilver*, crystallising in rhombic prisms. Artificially prepared calomel has been known from early times, and was used in the 16th century as a medicine under the names *Aquila alba*, or *Draco mitigatus*.

Mercurous chloride is formed by the union of its elements.

It may be prepared by addition of an alkaline chloride to a solution of mercurous nitrate or other mercurous salt. The precipitate is washed well to remove the alkaline chloride, which if allowed to remain would render the calomel slightly soluble. It may be prepared on the large scale by mixing 17 parts of corrosive sublimate with a little alcohol or water to prevent the escape of irritating fumes, and rubbing in 13 parts of mercury until *deadened.* The mixture is then sublimed in glass flasks, in the upper portion of which the calomel condenses as a solid, translucent, fibrous cake. The flasks are broken and the cake is removed, ground to a powder, washed repeatedly with boiling water to remove mercuric chloride, and dried. The powder has usually a slight yellowish tinge.

It is also prepared from the sulphate; 1 kilo. of mercury is mixed with 1·5 kilos of concentrated sulphuric acid in an iron boiler, gently heated until the fumes of sulphur dioxide cease to escape, and evaporated to dryness. It is then mixed with 1 kilo. of mercury and 1½ kilos of common salt until *deadened*, and is sublimed as usual.

Instead of condensing the calomel in a cake, the vapours may be led into chambers containing air or steam, in which it falls as a very fine powder, which requires no grinding. Sometimes the distillation is conducted in an iron tube connected with the condenser.

At Apothecaries' Hall, the proportions used are 62 parts of mercury sulphate, 40½ parts of mercury, and 34 parts of common salts.

The Japanese have long manufactured a very pure calomel, absolutely free from mercuric chloride, called '*keifun*' (light powder). Balls of porous earth and salt, soaked in 'bittern' (mother liquor of concentrated sea-water), are heated in iron pots lined with earth, each containing a little metallic mercury. Hydrochloric acid is formed from the magnesium chloride in the bittern, and the mercury distils into the closely fitting but unattached clay covers of the pots. Air enters by diffusion and the following reaction takes place:

$$4Hg+4HCl+O_2 = 2Hg_2Cl_2+2H_2O$$

by which calomel is formed at a temperature below its subliming point and fills the cover with a network of micaceous particles (Divers, J. Soc. Chem. Ind. 1894, 13, 108).

In preparing calomel by the wet way, 9 parts of mercury are digested in 8 parts of nitric acid (sp.gr. 1·2) with the aid of heat towards the end, until no more dissolves. The decanted solution is mixed with a boiling solution containing 8 parts of common salt in 64 parts of water and a few drops of hydrochloric acid. The precipitate is *well* washed with water. This form is said to be more effective for medicinal purposes than that prepared in the dry way.

Calomel is also produced by the action of reducing agents upon solutions of mercuric chloride.

Calomel may be obtained in a light voluminous form, which is 3 times as bulky as the samples prepared either by sublimation or by the usual precipitation methods, if the following prodecure is adopted. Three solutions are prepared containing (1) 11·5 grms. of mercuric chloride and 10 drops of hydrochloric acid in 100 c.c. of water; (2) 6 grms. of sodium bicarbonate and 10 grms of dextrose in 80 c.c. of water; (3) 7·5 grms. of crystalline magnesium chloride in 20 c.c. of water. Solutions (2) and (3) are mixed and added to (1). After the reaction has finished the mixture is heated on a water-bath until no more carbon dioxide is evolved, and the finely divided precipitate is collected and washed with cold water. In this form the calomel is stated to have much greater germicidal properties when used in prophylactic ointments or antisyphilitic injections than in the form as usually prepared (Duret, Ann. Inst. Pasteur. 1919, 33, 174; J. Soc. Chem. Ind. 1919, 338 A).

Calomel is a white, tasteless powder, of sp.gr. 6·56–7·41, crystallising in four-sided prisms terminating in pyramids. When heated it volatilises without previous fusion, giving a colourless vapour of sp.gr. 8·21 (air=1). This appears to indicate a molecular constitution HgCl, but Smith and Menzies (J. Amer. Chem. Soc. 1910, 32, 1541) have shown by quantitative measurements of vapour pressures that calomel vapour, even when saturated, is completely dissociated into mercury and mercuric chloride, and contains no molecules of the type HgCl or Hg_2Cl_2. The results also show that calomel is soluble in mercury and its molecular weight in that solution at 360°–400° corresponds to the monomolecular formula, HgCl. The boiling-point of calomel is 382·5° (For methods used *v.* S. and M. *ibid.* 32, 1419; *cp.* also Harris and V. Meyer, Ber. 1894, 27, 1482.) Baker states (Chem. Soc. Trans. 1900, 646) that perfectly dry mercurous chloride can be vaporised without dissociation and then has a v.d. corresponding to the formula Hg_2Cl_2. Further, by cryoscopic measurements, Beckmann has shown that mercurous chloride dissolved in fused mercuric chloride has the formula Hg_2Cl_2 (Zeitsch. anorg. Chem. 1907, 55, 175).

By conductivity measurements, the solubility of calomel in water has been found to be about 0·4 mgm. per litre at 20° (Ley and Heimbucher, Zeitsch. Elektrochem. 1904, 10, 301).

By treatment with alkalis and alkaline carbonates it is converted into mercurous oxide; ammonia converts it into 'black precipitate' NH_2Hg_2Cl. By digestion with ammonium chloride it is partially decomposed, mercuric chloride passing into solution and metallic mercury remaining undissolved (Richards and Archibald, Zeitsch. physikal. Chem. 1902, 40, 385). Hydrochloric acid or sodium chloride acts less rapidly. The prolonged action of steam, hot water, or hot air has a similar effect.

Calomel is largely used in medicine. The usual adulterations or impurities are corrosive sublimate, ammonium and sodium chlorides, lead and calcium carbonates and barium sulphate. The last three may be distinguished by their non-volatility, the others by their solubility in water or alcohol. According to Bonnewyn, if the calomel be shaken with a little alcohol the presence of even $\frac{1}{50000}$ part of corrosive sublimate can be detected by the black deposit produced on a knife-blade inserted into the solution.

Mercuric chloride, *Corrosive sublimate* $HgCl_2$. Mercury is converted into this salt when acted on by chlorine or *aqua regia.*

On the large scale it is prepared by distilling mercuric sulphate with common salt. Mercury is gently heated with concentrated sulphuric acid in an iron boiler until sulphur dioxide ceases to be evolved. The whole of the metal having dissolved, a slight excess of sulphuric acid is added to ensure the absence of mercurous sulphate, and a portion is tested by the addition of sodium chloride. If a precipitate of calomel falls, more acid is added. The mixture is evaporated and thoroughly dried. 20 parts of the sulphate is mixed intimately with 8 parts of sodium chloride and 1 part of manganese dioxide (to minimise the production of calomel) and introduced into glass subliming pots which are placed on iron plates, surrounded by sand to the necks and gently heated to remove moisture, which passes, through hoods placed over the necks, into a flue.

The moisture being removed, the hoods are replaced by small inverted conical condensers. Sufficient sand is then removed to uncover the upper half of the flasks, and the heat is increased until the whole has sublimed. The heat is finally raised sufficiently to render the sublimate coherent, but not to melt it. When cooled, the upper half of the flask is cracked away and the cake of sublimate is removed. On the lower part of the cake is frequently found a small quantity of the less volatile *calomel*; this is removed and added to a subsequent sublimation.

Wagner (Dingl. poly. J. 186, 135) recommends for the preparation on the large scale the decomposition of *turpeth mineral* (*v. Mercuric sulphate*) with hydrochloric acid. Mercuric chloride is thus obtained in a solution of sulphuric acid containing excess of mercuric oxide and is removed by crystallisation:

$$HgSO_4{\cdot}2HgO+2HCl=HgCl_2+H_2SO_4+2HgO$$

For the crude salt, he precipitates mercuric oxide by the addition of sodium hydroxide to mercuric nitrate and digests the precipitate with crude magnesium chloride (the mother-liquor from *carnallite*). Where the presence of potassium chloride is not injurious the carnallite itself may be used, in which case the crystals obtained on evaporation contain $KCl,HgCl_2,H_2O$.

Mercuric chloride occurs as a white, satiny, translucent mass, sp.gr. 5·403; or, when crystallised from solutions, as needles or four-sided prisms, belonging to the rhombic system (Mitscherlich, Pogg. Ann. 1833, 28, 118; Luczizky, Zeitsch. Kryst. Min. 1909, 46, 297). It fuses at 288° (Carnelley) and boils at 303° (Carnelley and Williams), giving a vapour of sp.gr. 9·8, corresponding to the normal molecular weight. The vapour condenses in triclinic crystals (Von Lang, Wien. Akad. Ber. 1862, 45, 119). The relations between the vapour pressures and the molecular volumes of the mercuric halides have been examined by Prideaux (Chem. Soc. Trans. 1910, 97, 2032).

100 parts of water dissolve at 10° 6·57 parts, and at 100° 53·96 parts of the salt. The solution is acid to test paper and gradually deposits calomel on exposure to light. Mercuric chloride is soluble in 3 parts of cold alcohol and in about 1·2 parts of boiling alcohol. It is soluble in 4 parts of cold ether and can be extracted from aqueous solution by this solvent. In aqueous solution, mercuric chloride undergoes electrolytic dissociation only to a very slight degree (Grotrian, Wied. Annalen, 1883, 18, 177; Luther, Zeitsch. physikal. Chem. 1904, 47, 107), but it is partially hydrolysed (Ley. Ber. 1897, 30. 2192). Sulphuric acid precipitates it from aqueous solution (Viard, Compt. rend. 1902, 135, 242), but it dissolves in the strong acid and in nitric acid without decomposition. Aqueous solutions of mercuric chloride decompose in the dark to form mercuric oxide, chlorine, and hydrochloric acid, or in the light to form only mercurous chloride and the acid (Verda, Chem. Zentr. 1907, i. 1392). Mercuric chloride is volatile with steam and the salt can be recognised in the vapour from its solutions by chemical tests, or by its action on a photographic plate (Kof and Haehn, Arch. Pharm. 1907, 245, 529; Zeitsch. physikal. Chem. 1907, 60, 367). The dry salt or its solution is easily reduced, first to calomel, and finally to metallic mercury, by arsenic, zinc, tin, &c.; or by stannous chloride, oxalic acid, hydrazine sulphate, or other reducing agents (*v. e.g.* de Coninck and Dautry, Bull. Acad. roy. Belg. 1908, 55).

Corrosive sublimate has a sharp, metallic taste, and is extremely poisonous. The best antidotes are egg-white, with which it forms an insoluble compound, or, in order of efficacy, sodium thiosulphate ('hypo'), hydrogen sulphide, sodium iodide, sodium bromide, and sodium chloride (Raimondi, Chem. Zentr. 1907, ii 1807). It is used in medicine both internally and externally, especially in cases of syphilis, and in surgery as an antiseptic in the form of dilute solutions (usually 1 : 100) and in gauzes and lint. (For the estimation of mercuric chloride in surgical dressing-materials, *see* Utz, Pharm. Post. 39, 785.) It is also used in preserving anatomical specimens and samples of milk, syrups, &c., for analysis.

Mercuric chloride forms numerous double salts and additive compounds. With the alkali chlorides it forms the compounds $KCl{\cdot}HgCl_2,H_2O$;

$$2KCl{\cdot}HgCl_2,H_2O;\quad KCl{\cdot}2HgCl_2,2H_2O$$

$2NaCl{\cdot}HgCl_2$; $NaCl{\cdot}HgCl_2,2H_2O$, and many others. Of the double salts with ammonium chloride only $HgCl_2{\cdot}2NH_4Cl,H_2O$ can be crystallised from water, but others are formed (Meerburgh, Zeitsch. anorg. Chem. 1908, 59, 136). To the formation of such compounds is due the increased solubility of mercuric chloride in solutions of alkali chlorides and in hydrochloric acid. In many cases, these solutions contain complex anions in which mercury is present (*v.* Sherrill, Zeitsch. physikal. Chem. 1903, 43, 705). It forms additive compounds with hydrocarbons, alcohols, and ketones, aromatic nitro derivatives (Mascarelli, Atti. R. Accad. Lincei, 1908, [v.] 17, i. 29), and with alkaloids. The latter compounds are frequently used in the purification of the alkaloids.

A series of *mercury oxychlorides* can be obtained from mercuric chloride by boiling its solution with mercuric oxide or by the action of potassium hydrogen carbonate or calcium carbonate upon it (Tarugi, Gazz. chim. ital. 1901, 31, ii. 313; Arctowski, Zeitsch. anorg. Chem. 1896, 12, 353; Driot, Compt. rend. 1911, 152, 958). $2HgCl_2{\cdot}HgO$ crystallises in red monoclinic needles; $HgCl_2{\cdot}HgO$ amorphous yellow powder; $HgCl_2{\cdot}2HgO$ is a black crystalline precipitate, and $HgCl_2{\cdot}3HgO$ occurs in glistening yellow scales as the mineral *kleinite* (Sachs, Sitzungsber. K. Akad. Wiss. Berlin, 1905, 1091). Hewitt states that when caustic soda solution diffuses into a solution of mercuric chloride and sodium chloride, very dark red crystals of the formula $Hg_6O_5Cl_2$ are produced (Chem. Soc. Proc. 1907, 23, 10; *v.* also Buttle and Hewitt, Chem. Soc. Trans. 1908, 93, 1405).

Mercurous bromide Hg_2Br_2 is obtained as a white precipitate by adding a soluble bromide to a solution of a mercurous salt, or by the prolonged action of bromine water on the metal. It crystallises from mercurous nitrate solution in white, pearly, tetragonal leaflets. sp.gr. 7·037, and is nearly insoluble in water. At 340°-350° it sublimes without decomposition.

Mercuric bromide $HgBr_2$ is formed from its elements with evolution of heat (Nernst, Zeitsch. physikal. Chem. 1888, 2, 20; Varet, Compt. rend. 120, 620), and is produced by dissolving mercuric oxide in hydrobromic acid. Cold water dissolves 0·4 p.c. and boiling water 2·5 p.c. of the salt, and on cooling it crystallises out in anhydrous glistening scales. From alcohol it crystallises in white rhombic prisms. Mercuric bromide melts at 244° (Carnelly and Williams, Chem. Soc. Trans. 1880, 127) (235° is given for m.p. by Guinchant, Compt. rend. 1909, 149, 479). Like the chloride it is decomposed by boiling with water, *oxybromides* being formed (Fischer and Wartenburgh, Chem. Zeit. 1902, 26, 966).

It is occasionally administered in medicine instead of mercuric chloride, usually by hypodermic injection of a solution of the soluble compounds with sodium chloride $HgBr_2 \cdot 2NaCl$ or bromide $HgBr_2 \cdot 2NaBr$ (Vicario, J. Pharm. Chim. 1907, [vi.] 26).

A double bromide of mercury and potassium has been used as a disinfectant (Cooke, Eng. Pat. 1530, 1905).

Mercurous iodide Hg_2I_2 is a green insoluble powder employed medicinally. It is prepared by triturating a mixture of 5 parts iodine and 8 parts mercury, moistened with alcohol; or by precipitation of a mercurous salt with potassium iodide. A purer product, obtained by boiling excess of iodine with a solution of mercurous nitrate containing nitric acid, crystallises in transparent, yellow, tetragonal plates, blackened by light. When heated it becomes first yellow, then red and finally garnet-red, and on cooling passes through the same colour changes in reverse order. It begins to sublime at about 190° and at 290° melts with decomposition (Stroman, Ber. 1887, 20, 2818; François, J. Pharm. Chim. 1899, [vi.] 10, 16; Compt. rend. 1895, 121, 888; 1896, 122, 190). It dissolves slightly in various oils. The best solvent is castor oil, of which 100 parts dissolves 2 parts of the iodide.

Mercuric iodide HgI_2. A mixture of 5 parts iodine and 4 parts mercury is moistened with a little alcohol, triturated, and sublimed. Dublanc pours 1 kilo. of alcohol upon 100 grams of mercury and adds 124 grams of iodine in 10 successive portions, triturating each time until the alcohol becomes colourless. The last 4 grams usually produce a permanent colour. The precipitate is then washed with alcohol and dried.

In the wet way, which is the best, a solution of 10 parts potassium iodide is added to a solution of 8 parts mercuric chloride, and the precipitate, which is salmon-coloured at first but soon becomes red and crystalline, is washed. A slight excess of either the chloride or iodide will redissolve a portion of the precipitate.

Mercuric iodide may be obtained in comparatively large crystals by the action of a mercuric salt on ethyl or methyl iodides (Bodroux, Compt. rend. 130, 1622); by the action of these iodides on the metal a very pure product may be obtained (Neogi, Chem. Soc. Abstr. 1907, ii. 772).

Mercuric iodide is dimorphous, existing in a red and a yellow form. The *red* variety is produced by the above methods of preparation. It crystallises from hot potassium iodide, alcohol, or nitric acid in tetragonal prisms and pyramids (Luczizky, Zeitsch. Kryst. Min. 1909, 46, 297), and is soluble in many organic solvents (Beckmann and Stock, Zeitsch. physikal. Chem. 1895, 17, 130). Its sp.gr. is 6·26. When heated to 127° it changes into the *yellow* modification with absorption of heat (Guinchant, Compt. rend. 1907, 145, 68). If further heated it remains yellow up to 190°, but slowly becomes red again, the colour deepening continuously between 180° and 255·5° when it melts (Rodwell, Phil. Trans. 1882, 173, 1125; Smits and Bokhorst, Zeitsch. physikal. Chem. 1915, 89, 365). Observations made with large crystals of yellow mercuric iodide show that the gradual development of the orange colour with rise of temperature is not accompanied by any change in crystalline form. This fact points to the formation of mixed rhombic crystals containing both yellow and red modifications. There are apparently two isomeric forms of mercuric iodide (α and β), the red and yellow modifications being mixed crystals containing the two forms in different proportions (Smits, Proc. K. Akad. Wetensch, Amsterdam, 1917, 19, 703). The yellow form volatilises without decomposition, the vapour density corresponding to the formula HgI_2. By cooling the liquid or condensing the vapour (Gernez, Compt. rend. 1899, 128, 1516), the yellow modification is obtained in rhombic prisms of sp.gr. 6·06 which retain their form and colour when cooled to the ordinary temperature, but slowly (or immediately on rubbing) pass into the red variety. Nevertheless the yellow form may be kept at the ordinary temperature for many years (Gernez, Compt. rend. 1909, 148, 1015), and it separates from nearly all organic solvents in this form, though it is only stable above 126° (Kastle and Clark, Amer. Chem. J. 1899, 22, 473; Kastle and Reed, *ibid.* 1902, 27, 209; Gernez, Compt. rend. 1903, 136, 889; 129·5° Reinders, Zeitsch. physikal. Chem. 1900, 32, 507). If mercuric iodide is heated at about 300°–500° in a long glass tube connected with a vessel in which the pressure can suddenly be decreased from 1 to $\frac{1}{10}$th atmosphere it condenses as *colourless* snow which becomes pink and ultimately red (Tamman, Zeitsch. anorg. Chem. 1920, 109, 213). 1 litre of absolute alcohol at 18° dissolves 11·18 grams of the salt; 80 p.c. alcohol dissolves only 2·86 grams. It is almost insoluble in water; 1 litre at 17·5° dissolves 0·0403 gram (Bourgoin, Bull. Soc. chim. [ii.] 42, 620).

In potassium or other alkaline iodide, it dissolves freely with formation of a double iodide.

The solution in potassium iodide is a more powerful antiseptic than mercuric chloride. It has been employed in the preparation of an antiseptic soap (Thomson, J. Soc. Chem. Ind. 1888, 192). An alkaline solution of mercuric iodide in potassium iodide is employed as a delicate test for ammonia and its compounds, being known as *Nessler's solution.*

In mercuric chloride it dissolves readily, forming a double chloride and iodide.

Mercuric iodide forms a very large number of double salts (*v.* Duboin, Ann. Chim. Phys. 1909, [viii.] 16, 258). With alkali iodides and ether it forms both crystalline and liquid compounds, *e.g.* $KHgI_3 \cdot 3Et_2O$, and $KHgI_3 \cdot 4Et_2O$ (Marsh. Chem. Soc. Trans. 1910, 2297).

Mercuric iodide is much used in photography as an intensifier, a solution in sodium sulphite containing the proportions, $HgI_2 : Na_2SO_3$: water : : 1 : 10 : 100, being the best. For details *see* Lumière Bros. and Seyewetz (Monit. Scient. 1899, 13, 782 ; J. Soc. Chem. Ind. 1899, 1155).

Mercurous fluoride Hg_2F_2, produced by the action of hydrofluoric acid on the carbonate or of silver fluoride on calomel (Finkener, Pogg. Ann. 110, 142), is a yellow crystalline powder, hydrolysed by hot water and blackened by light.

Mercuric fluoride $HgF_2,2H_2O$, prepared by dissolving mercuric oxide in aqueous hydrofluoric acid (Finkener, Pogg. Ann. 110, 628) is a white crystalline salt. It is decomposed in air at 50° forming an *oxyfluoride* $HgF(OH)$; and in dilute aqueous solution is completely hydrolysed, but without formation of oxyfluorides (Jaeger, Zeitsch. anorg. Chem. 1901, 27, 22; Cox, *ibid.* 1904, 40, 146)

Anhydrous mercuric fluoride may be prepared by heating mercurous fluoride in dry chlorine at 275°, or in dry bromine at 400°, or by heating mercurous fluoride at 450° under 10 mm. pressure. Transparent octahedral crystals, m.p. 645°, b p. 650° (estimated). On exposure to air hydrogen fluoride is evolved and mercuric oxyfluoride and ultimately mercuric oxide are formed.

Mercuric chlorofluoride Hg_2ClF, a pale yellow substance, formed by passing dry chlorine over mercurous fluoride at 120° (Ruff and Bahlau, Ber. 1918, 51, 1752).

Mercurous sulphate $Hg_2(SO_4)_2$ is prepared by dissolving 2 parts mercury in 3 parts sulphuric acid with the aid of a gentle heat; or by the addition of sulphuric acid to a solution of mercurous nitrate; or by the electrolysis of sulphuric acid with a mercury anode (Hulett, Zeitsch. physikal. Chem. 1904, 49, 494). It is a white crystalline salt which with water yields first the basic salt $Hg_2SO_4 \cdot Hg_2O,H_2O$, and finally the oxide.

Mercurous sulphate is used in the standard cells of Clark and Weston.

Mercuric sulphate $HgSO_4$ is prepared by dissolving mercury in strong sulphuric acid with the aid of heat, or mercuric oxide in dilute sulphuric acid. Its preparation has been described under *Mercuric chloride.*

From its solution in sulphuric acid it crystallises in small, silvery, stellate plates. When strongly heated, it becomes reduced to mercurous sulphate with evolution of oxygen, mercury, and sulphur dioxide.

It is soluble in sodium chloride solution. When heated with water it produces a yellow basic sulphate $HgSO_4 \cdot 2HgO$, which turns red when heated, known as *turpeth* or *turbith mineral,* which is soluble in 2000 parts of cold and 600 parts of hot water. Turpeth appears to be the only basic sulphate which can exist in equilibrium with water at 25° (Cox, Zeitsch. anorg. Chem. 1904, 40, 165; Hoitsema, Zeitsch. physikal. Chem. 1895, 17, 651: Guinchant, Bull. Soc. chim. 1896, [iii.] 15, 555). A thiobasic mercuric sulphate, $4HgO \cdot 2HgS \cdot 3SO_3,4H_2O$, has been described by Estrup (Zeitsch. anorg. Chem. 1909, 62, 168).

Nitrates. Several nitrates of mercury are known. When excess of mercury is dissolved in a cold mixture of 1 part nitric acid and 4 parts water, the *mercurous* salt is formed. If the acid be sufficiently strong to effervesce, or be used in excess, or if the mixture be heated, *mercuric* nitrate is produced.

Mercurous nitrate $Hg_2(NO_3)_2$ forms monoclinic tables containing 2 molecules of water. They effloresce and become anhydrous in dry air and when heated to 70° melt to a clear liquid of sp gr 4·3 (Retgers, Jahrb Min. 1896, ii. 183). The pure salt is immediately decomposed by water with formation of a basic nitrate, and when it is boiled with water mercury is volatilised and may be condensed in globules (Hada, Chem. Soc Trans. 1896, 1667). Several basic nitrates are known (*v.* Cox, Zeitsch. anorg. Chem. 1904. 40, 174).

Mercuric nitrate $Hg(NO_3)_2$ is produced by boiling mercury with nitric acid until the solution no longer gives a precipitate with sodium chloride. Large crystals containing

$$2Hg(NO_3)_2,H_2O$$

separate on concentration.

The action of water at 25° on mercuric nitrate produces a basic salt, $Hg(NO_3)_2 2HgO$, as a heavy white powder, which is decomposed on further treatment with water yielding the oxide (Cox, Zeitsch. anorg. Chem 1904, 40, 159).

Mercurous nitrite $Hg_2(NO_2)_2$ is produced by the action of dilute nitric acid upon mercury and forms yellow needles which are partially decomposed by water. Dilute nitric acid slowly converts it into mercurous nitrate, and when heated it decomposes yielding nitric oxide, mercurous nitrate, mercury, and mercuric oxide (Rây, Zeitsch. anorg. Chem. 1896, 12, 365; Chem. Soc. Trans. 1897, 337; Rây and Sen, *ibid.* 1903, 491). The pure salt has sp.gr. 5·925 (Rây, Chem. Soc. Trans. 1908, 999).

Mercuric nitrite $Hg(NO_2)_2$ is obtained by the action of mercuric chloride on silver nitrite or by the decomposition of mercurous nitrate by water (Rây, Chem. Soc. Proc 20, 57; Chem. Soc. Trans. 1897, 71, 337).

Mercuric hyponitrite HgN_2O_2, formed by the action of sodium hyponitrite on mercuric nitrite, is a buff-coloured powder which decomposes spontaneously into nitric oxide and mercurous hyponitrite (Divers, Chem. Soc. Trans. 1899, 119; *see also* Rây, *ibid.* 1907, 1404, 2031; Rây and Gañguli, *ibid.* 1399).

Mercury nitride N_2Hg_3 is produced as a brown powder by the action of potassamide on mercuric bromide in liquid ammonia solution. When dry it is very explosive (*v.* Franklin, Zeitsch anorg. Chem. 1905, 46, 1).

Mercury acetylide (*mercury carbide*)

$$ClHg\,HC:CHCl$$

prepared by passing acetylene into a solution of mercuric oxide in ammonium hydrate and carbonate, is a heavy white powder, which is explosive (*v.* Plimpton and Travers, Chem. Soc. Trans. 1894, 264). For the action of acetylene on solutions of mercuric chloride and acetate, *see* Burkard and Travers (Chem. Soc. Trans. 1902, 81, 1271); Biltz and Mumm (Ber. 1904, 37, 4417), and Brame (Chem. Soc. Trans. 1905, 427). Chapman and Jenkins (*idem.* 1919, 115, 847). An acetylide containing twice the amount of acetylene, and having the constitution

$$CHCl:CH \cdot Hg \cdot CH:CHCl$$

has been prepared by Jenkins (Chem. Soc. Trans 1921, 119, 747).

Mercuric cyanide $Hg(CN)_2$ is prepared by boiling a solution of 1 part potassium ferrocyanide and 2 parts mercuric sulphate in 7 parts water:

$$2K_4Fe(CN)_6+7HgSO_4 = 6Hg(CN)_2+4K_2SO_4+Fe_2(SO_4)_3+Hg$$

It may also be prepared by adding 31 grams sodium cyanide dissolved in 50 c.c. water to 90 grams mercuric sulphate. Heat is evolved and the whole solidifies to a mass of granular mercuric cyanide which is extracted with boiling alcohol and finally recrystallised from water (Rupp and Goy, Apoth. Zeit. 1908, 23, 374).

It crystallises in white needles or tetragonal prisms soluble in 8 parts of cold water, insoluble in absolute alcohol. When ignited, it decomposes with evolution of cyanogen.

In aqueous solution mercuric cyanide only undergoes ionic dissociation to a very small extent, and therefore does not exhibit all the usual reactions of mercuric salts. For example, with potassium iodide it yields, not mercuric iodide, but a complex salt $Hg(CN)_2{\cdot}HgI_2{\cdot}2KCN$ (Rupp and Goy, Arch. Pharm. 1909, 247, 100). It is decomposed with formation of hydrocyanic acid by hydrochloric, hydrobromic, and hydriodic acids, or by sulphuretted hydrogen, but not by dilute sulphuric or nitric acids.

The aqueous solution readily dissolves mercuric oxide forming the basic salt $Hg(CN)_2{\cdot}HgO$, which is used as an antiseptic under the name of *mercuric oxycyanide* (Holdermann, Arch. Pharm. 1905, 243, 600; 1906, 244, 133; Rupp, *ibid.* 1906, 244, 1; Jones, Pharm. J. 1920, 105, 87). The pure salt is dangerous to handle and may occasion explosions.

Mercuric thiocyanate $Hg(CNS)_2$ is prepared by the addition of an excess of mercuric chloride to a solution of ammonium thiocyanate. It forms a white crystalline precipitate which burns freely when ignited with evolution of mercurial vapours, and forms a most voluminous ash.

It is occasionally made into a thick paste with gum and worked into pilules which when dried are sold as *Pharaoh's serpent's eggs*.

It is soluble in a solution of ammonium thiocyanate, and this solution, under the trade-name 'Agfa,' is used as an intensifier for photographic negatives (Eberhard, Photo. Mittheil, 1901, 38, 15; J. Soc. Chem. Ind. 1901, 387).

Ammoniacal Compounds of Mercury.

Very many of these compounds have been described, but little is known as to their constitution because the ordinary methods for the determination of molecular weight are not applicable to them.

It is probable that there exist substitution products of ammonia of the type $(OHg_2)NH_2{\cdot}X'$ (*amino-mercuric compounds*); substitution products of ammonium compounds of the type

$$NHg_2X'{\cdot}H_2O$$

mercuri-ammonium compounds); and additive compounds of ammonia and mercuric salts. (*See* Rammelsberg, J. pr. Chem. 1888 [ii.] 38, 558; Barfoed, *ibid.* 1889, [ii.] 39, 201; Pesci, Gazz. chim. ital. 1891, 21, 569; Zeitsch. anorg. Chem. 1899, 21, 301; *see also* Hofmann and Marburg, Annalen, 1899, 305, 198; Zeitsch. anorg. Chem. 1900, 23, 126; Franklin, J. Amer. Chem. Soc. 1907, 29, 35).

Millon's base has the empirical formula $H_5O_3NHg_2$, and is regarded as *dihydroxydimercuriammonium hydroxide* $(HO{\cdot}Hg)_2:NH_2{\cdot}OH$, or as dimercuriammonium hydroxide

$$NHg_2{\cdot}OH{\cdot}2H_2O$$

It is formed as a pale yellow powder when mercuric oxide is gently warmed with dilute ammonia. It deflagrates when heated.

Salts of Millon's base are formed by digesting the base with dilute acids, or by adding ammonia to solutions of mercuric salts of oxyacids. Anhydrous salts of the formula NHg_2X' have been obtained but are probably not true derivatives of Millon's base, but amino compounds of the type $Hg:N{\cdot}HgX'$ (Franklin, Zeitsch. anorg. Chem. 1905, 46, 1; *see also* François, Compt. rend. 1900, 130, 332, and 1022).

The iodide of Millon's base $(OHg)_2NH_2{\cdot}I$ (*oxydimercuriammonium iodide*) is formed by adding ammonia to a solution of mercuric potassium iodide (Nessler's solution, *v.* ANALYSIS), or by the action of excess of ammonia on mercuric iodide. It is a brown powder, fusible without decomposition

Amino-mercuric chloride, *Infusible white precipitate* $H_2N{\cdot}HgCl$ (Hofmann and Marburg; Franklin; Saha and Choudhury, Zeitsch. anorg. Chem. 1914, 86, 225), is prepared by the addition of ammonia to a solution of mercuric chloride. For medicinal purposes 1 ounce of mercuric chloride is dissolved in 3 quarts of water, and to the cool solution 8 fluid ounces of concentrated ammonia is added with frequent agitation, and the precipitate is washed and dried.

It is a white, inodorous, highly poisonous powder, totally volatile on heating to 360°, slightly soluble in boiling water, easily soluble in nitric, hydrochloric and sulphuric acids, insoluble in alcohol.

An analogous compound derived from ethylamine, $NH(C_2H_5)HgCl$, is known.

By digesting infusible white precipitate with nearly saturated solutions of ammonium chloride containing varying amounts of mercuric chloride, compounds of the formula $3HgCl_2{\cdot}2NH_3$ or of $HgCl_2{\cdot}2NH_3$ separate out. By using solutions nearly saturated with mercuric chloride and adding variable small amounts of ammonium chloride $HgCl_2{\cdot}NH_2{\cdot}HgCl$ is formed (Strömholm) (Holmes, Chem. Soc. Trans. 1918, 113, 74).

Fusible white precipitate $Hg(NH_3)_2Cl_2$ is produced by boiling the above compound with ammonium chloride solution, and form crusts of small regular dodecahedra.

Mercury Salts of Organic Acids.

Mercurous formate $Hg_2(HCO_2)_2$, obtained by adding sodium formate to mercurous nitrate solution, forms white leaflets soluble in 250 parts of water at 17°. When boiled with water it is reduced to metallic mercury (Liebig, Annalen, 3, 207).

Mercuric formate $Hg(HCO_2)_2$, obtained by solution of yellow mercuric oxide in dilute formic acid, slowly changes to mercurous formate with liberation of formic acid and carbon dioxide (Varet, Compt. rend. 1905, 140, 1641).

Mercurous acetate $Hg_2(CH_3\cdot CO_2)_2$ forms white leaflets, more stable than the formate, soluble in 133 parts of water at 12°–15° (Lefort, Annalen, 56, 247).

Mercuric acetate $Hg(CH_3\cdot CO_2)_2$ also forms white leaflets soluble in 2·75 parts of water at 19° and in 1 part at 100°. The aqueous solution is acid, and on warming, the salt is largely hydrolysed. Both these salts are used in medicine for the treatment of skin diseases.

Mercuric benzoate is obtained by precipitation from sodium benzoate and a mercuric salt; it cannot be recrystallised from water, as it is very slightly soluble, and undergoes partial hydrolysis.

Mercuric oleate and **stearate**, prepared by double decomposition, are used in pharmacy (Dott, Chemist and Druggist, 1909, 74, 785).

Mercurous oxalate $Hg_2C_2O_4$ is a white salt, very slightly soluble in water, insoluble in excess of oxalate (Schafer and Abegg, Zeitsch. anorg. Chem. 1905, 45, 299). It has been used in gelatin emulsions for phototype printing (Castellani, Phot. Korr. 1906, 43, 281; J. Soc. Chem. Ind. 1906, 827).

Mercuric oxalate HgC_2O_4 is also sparingly soluble in water, but forms soluble double salts with many oxalates. In solution it is quantitatively reduced to mercurous oxalate by the action of light (Roloff, Zeitsch. physikal. Chem. 1894, 13, 324). This reaction is made use of in *Eder's mercury oxalate photometer* (*v.* Abegg, Zeitsch Elektrochem. 1903, 9, 569). The sensitiveness of the solution to light is increased by the fluoresceins and their sodium salts (Jodlbauer and Tappeiner, Ber. 1905, 38, 2602).

Mercuric fulminate $(C:N\cdot O)_2Hg,\frac{1}{2}H_2O$ is prepared by adding 17 parts of alcohol (90 p.c.) to a cold solution of 3 parts of mercury in 36 parts of nitric acid (sp.gr. 1·34), contained in a large flask. The mixture froths and turns black, and a very violent reaction takes place which is moderated by the addition of another 17 parts of alcohol. On the large scale the reaction is carried out by mixing in large glass balloons 1 part of mercury, 10 parts of nitric acid (sp gr. 1·33), and alcohol (sp.gr. 0·833) in the proportion of 1 litre to each kilo. of acid. The reaction generally begins spontaneously and is allowed to proceed by itself (Beckmann, Ber. 1886, 19, 993; Lobry de Bruyn, *ibid.* 1370) (*v.* FULMINIC ACID).

On cooling the solution produced by either method, mercuric fulminate crystallises in shining white or grey-coloured prisms, sp.gr. 4·42. It is insoluble in cold water, but fairly soluble in hot water and in aqueous ammonia (*v.* Steiner, Ber. 1876, 9, 779).

Pure mercury fulminate is unacted upon by potassium permanganate, and the presence and amount of unsaturated impurities in the salt may be determined by its behaviour towards permanganate (Rathsburg, Ber. 1821, 54 [B], 3185).

Mercuric fulminate explodes violently on percussion or when treated with sulphuric acid, and is much used as a detonator (*v.* EXPLOSIVES): but when ignited with a flame it burns with a reddish flame yielding carbon monoxide, nitrogen, and mercury.

Mercuric Azide HgN_6 may be obtained by mixing concentrated solutions of sodium azide and mercuric nitrate, when mercuric azide is precipitated as a powdery mass which can be purified by solution and crystallisation. It is highly explosive. Although it has the same molecular weight as mercuric fulminate and develops the same volume of gas on detonation, its 'brisance' is twenty to thirty times as great (*cf.* Stettbacher, Zeitsch. ges. Schiess. u. Sprengstoffw. 1920, 15, 211). *See* EXPLOSIVES.

Mercury gallate, prepared by triturating 37·6 grams gallic acid and 21·6 grams yellow mercuric oxide in 25 c.c. of water, is used therapeutically as an antisyphilitic (Brousse and Gay, Compt. rend. 1893, 117, 284).

Mercury tannate is prepared by triturating mercurous nitrate (20 grams) with tannin (12 grams), and is also used in medicine (Zdarck, J. Pharm. d'Anvers, 58, 98).

Mercuric ***p*****-phenolsulphonate** is used medicinally under the name '*hydrargyrol*,' and its compound with ammonium tartrate is similarly used and known as '*asterol*.'

ORGANIC MERCURY DERIVATIVES.

Mercury can replace hydrogen in most organic compounds, and the substances so formed fall into two broad classes: (*a*) those in which mercury is attached to carbon, and (*b*) those in which it is attached directly to nitrogen. Generally, compounds of class (*a*) are non-electrolytes and in general chemical properties resemble the parent compounds. Compounds of class (*b*) are usually less stable and in solution show the reactions of the mercuric ion.

Mercury Derivatives of Aliphatic Compounds.

Mercury alkyl derivatives are of two classes:

(1) Monalkyl derivatives

$$X\cdot Hg\cdot C_nH_{2n+1} (X = Cl, Br, I, \text{etc.})$$

(2) Dialkyl derivatives $Hg(C_nH_{2n+1})_2$.

(1) *Monalkyl mercury compounds* are prepared:

(*a*) By the action of mercury on alkyl iodides in sunlight.

(*b*) By the action of halogens, haloid acids, or mercury halides on the dialkyl derivatives.

The halogen compounds are usually colourless crystalline solids, which have a definite melting-point and can be sublimed and distilled in steam. Treated with moist silver oxide they yield hydroxy compounds which are thick liquids, soluble in water and alcohol, strongly basic in character and forming series of salts.

Methyl mercuric iodide $CH_3\cdot HgI$, forms colourless crystals, m.p. 143°, which sublime when heated (Frankland, Annalen, 85, 361).

Ethyl mercuric chloride $C_2H_5\cdot HgCl$ forms pearly leaflets, sp.gr. 3·48, subliming at 40° (Dunhaupt, Annalen, 92, 379; *see also* Buckton, *ibid.* 112, 221).

Ethyl mercuric hydroxide $C_2H_5\cdot HgOH$, produced by the action of moist silver oxide on the preceding compound, is a viscous caustic liquid which gives rise to a number of salts.

(2) *Mercury dialkyls* are prepared:

(*a*) By the action of sodium amalgam on alkyl iodides in presence of ethyl acetate (Frankland, Annalen, 130, 105).

(*b*) By the action of potassium cyanide on mercury alkyl iodides.

(c) By treating zinc alkyls with mercuric chloride or an alkyl mercuric chloride (*v. also* Buckton, *ibid.* 108, 103).

They are colourless heavy liquids, unchanged by air or water at the ordinary temperature. They have a peculiar faint odour, and are extremely poisonous (*v.* Hepp, Ber. 1887, Ref. 798). When heated in air they burn.

Mercury dimethyl $Hg(CH_3)_2$ has b.p. 93°–96° and sp.gr. 3·07. Hydrochloric acid converts it into mercuric chloride (Seidel, J. pr. Chem. [ii.] 29, 134).

Mercury diethyl $Hg(C_2H_5)_2$ has b.p. 159°, sp.gr. 2·44. Mixed mercury alkyls of the type $CH_3 \cdot Hg \cdot C_2H_5$, have not been obtained (Frankland, Annalen, 111, 57; Buckton, *ibid.* 109, 222).

(For an account of the many known aliphatic compounds containing mercury, *see* Beilstein's Handbuch der Org. Chem. Bd. i. 1524–1526; suppl. i. 854).

Mercuriethylene-diamine sulphate

$$Hg(CH_2 \cdot NH_2)_2 \cdot H_2SO_4$$

mixed with a molecular proportion of ethylene diamine is used as an antiseptic under the trade name '*sublamin.*' It does not precipitate soap, or coagulate albumen, and has a greater germicidal and a less toxic action, weight for weight, than mercuric chloride (Scordo, Chem. Soc. Abstr. 1907, ii. 713; Pesci, Gazz. chim. ital. 1909, 39, i. 143).

Mercury Derivatives of Aromatic Compounds.

Aryl mercuric compounds are formed with an ease comparable with that of sulphonation or nitration and the metal enters the usual position in the molecule (except in the case of benzoic acid, *v.i.*). They are usually prepared by boiling the aryl compounds with mercuric chloride solution. When acted on by stannous chloride in alkaline solution they yield mercury and mercury aryls of the type HgR_2 (Dimroth, Chem. Zentr. 1901, i. 449).

Mercury diphenyl $Hg(C_6H_5)_2$ is prepared by heating bromobenzene, mercuric chloride, and metallic sodium in benzene (Michaelis and Reese, Ber. 1882, 2876); or by heating bromobenzene with an equal volume of xylene, a little ethyl acetate and excess of sodium amalgam (Aronheim, Annalen, 194, 145). It is also obtained by the action of mercuric chloride on an ethereal solution of magnesium phenylbromide (Pfeiffer and Truskier, Ber. 1904, 37, 1125). It crystallises from benzene in white needles or rhombic prisms, m.p. 125°–126°, is easily volatile and gives a vapour irritating to the eyes. Mercury diphenyl has a therapeutic action equal to that of the fatty compounds, but it is less poisonous (Louise and Moutier, Compt. rend. 1905, 140, 1703).

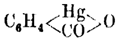
Phenyl-mercuric chloride $C_6H_5 \cdot HgCl$, made by the action of chlorine on mercury diphenyl, forms small white rhombic prisms, m.p. 250° (Dreher and Otto, Annalen, 154, 93).

Phenyl-mercuric hydroxide $C_6H_5 \cdot HgOH$ is a strongly caustic liquid and forms numerous salts (Otto, Ber. 1885, 246).

Mercury di-tolyls, di-xylyls, di-naphthyls, &c., are known, and each forms similar series of compounds.

o- and *p-Hydroxyphenyl mercurioxides* and *hydroxy-phenylene-dimercuryoxides* are present in the so-called 'mercury phenate,' the *hydrargyrum carbolicum*—of the pharmacopœias (Dimroth, Ber. 1902, 35, 2853). This is obtained by precipitating a solution of mercuric chloride with sodium phenate (Merck, Apoth. Zeit. 1889, 4, 651; Andres, Pharm. Zeitsch. Russe, 27, 625), and is used medicinally in the treatment of syphilis.

o-Hydroxymercuribenzoic anhydride

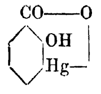


$$C_6H_4 {<}{\substack{Hg \\ CO}}{>} O$$

is the chief constituent of the 'mercury benzoate' used medicinally. It is prepared by digesting freshly precipitated mercuric oxide with benzoic acid and water and is formed by the action of dilute acids on the salts of *o-hydroxymercuribenzoic acid* $C_6H_4 {<}{\substack{Hg \cdot OH \\ CO \cdot OH}}$.

o-Mercuridibenzoic acid $Hg:(C_6H_4 \cdot COOH)_2$ is also known (Pesci, Atti. R. Accad. Lincei, [v.] 10, i. 413).

Anhydro-o-hydroxymercurisalicylic acid



is produced by boiling mercury salicylate with water for 15 minutes, and is therefore the main constituent of '*hydrargyrum salicylicum,*' which is prepared by digesting yellow mercuric oxide with aqueous salicylic acid. It is much used in the treatment of syphilis (Buroni, Gazz. chim. ital. 32, ii. 307; Dimroth, Ber. 35, 2872; *see also* Larin, Chem. Zeit. Rep. 1901, 25, 193).

(For further details of mercury aromatic compounds and a complete bibliography, *v.* Beilstein, Handbuch der Org. Chem. Bd. iv 1703–1713; suppl. iv. 1208–1218.

MERGAL. Trade name for a combination of mercury cholate and albumin tannate.

MERIODIN. *Meriodin* is a trade name for mercury diiodo-para-phenolsulphonate; it is also known as 'mercury sozoiodol.' It is a caustic, and has been used as an antisyphilitic. It is an orange-yellow powder, soluble in sodium chloride solution, but insoluble in water or alcohol. It is employed in parasitic and syphilitic skin diseases, and as a dusting powder in intertrigo, leg ulcers, &c. '*Anogon*, a mixed mercurous and mercuric compound of diiodophenol sulphonic acid ('Sozoiodol'), is also called Meriodin.'

MERLUSAN. Trade name for a mercury compound of tyrosine.

MEROCHINOL. Trade name for mercury hydroxyquinoline sulphonate.

MESCAL BUTTONS *v.* Mezcaline.

MESITITE. A member of the calcite group of minerals intermediate in composition between magnesite and chalybite. Rather than having the definite molecular composition $2MgCO_3 \cdot FeCO_3$ assigned to it by Breithaupt, it is an isomorphous mixture of 50–70 p.c. $MgCO_3$ and 50–30 p.c. $FeCO_3$, grading on the one side through breunnerite into magnesite, and on the other through pistomesite and sideroplesite into chalybite. Sp.gr. 3·3–3·45. It occurs as well-developed, pale yellow, rhombohedral crystals in the iron mines at Traversella in Piedmont, and as sparry masses in the Styrian magnesite (breunnerite) deposits. L. J. S.

MESITOL *v.* Phenol and its homologues.

MESITYLENE *v.* Cumenes.

MESORCINOL *v.* Phenol and its homologues.

MESOTAN. Trade name for a yellowish oily liquid, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}OCH_2{\cdot}OCH_3$, obtained by treating sodium salicylate with monochlordimethyl ether (*v.* Synthetic drugs).

MESO-THORIUM *v.* Radioactivity and Thorium.

MESOXALDIALDEHYDE *v.* Ketones.

MESOXALIC ACID *v.* Ketones.

META-ARABIC ACID *v.* Gums.

METACETONE. By heating sugar with lime Fremy obtained a substance, b.p. 84°, to which he gave the name *metacetone* and the formula $C_6H_{10}O$. Fischer and Laycock find that this body is in reality a mixture of *propylaldehyde*, *dimethylfurfuran*, a third substance with the properties of a hydrocarbon, and a number of other lower and higher boiling homologues. Fischer and Laycock distilled 100 kilos. of sugar and 300 kilos. of burnt lime, and collected the distillate in fractions. Fraction *a*, distilling below 65°, combined partly with phenylhydrazine, yielding the phenylhydrazone of propylaldehyde. The distillate boiling at 25°–45°, consisted of furfuran, and that boiling at 45°–65° is probably methylfurfuran. Fraction *b*, distilling at 65°–115°, was treated like fraction *a*, phenylhydrazine being added, and the product distilled. The distillate consisted of a hydrocarbon and a substance which dissolved on heating with dilute hydrochloric acid to 170°, forming acetonylacetone, and which is probably dimethylfurfuran. The residue, which combined with phenylhydrazine is the phenylhydrazone of propylaldehyde. The fraction boiling above 115° is a complex mixture, consisting of higher homologues of furfuran and aldehydes, which could be removed with sodium bisulphite.

Fischer and Laycock have investigated wood tar, and found that this likewise contains propylaldehyde and dimethylfurfuran (Ber. 1889, 22, 101).

METACETONIC ACID *v.* Propionic acid.

METAHEWETTITE *v.* Hewettite.

METALDEHYDE *v.* Aldehyde.

METALLIC SOAPS *v.* Soaps.

METALLOGRAPHY deals with the internal structure and constitution of metals and their alloys. The science is a comparatively young one, dating back only to 1864, when Sorby (Proc. Sheffield Lit. Phil. Soc. 1864) first applied the microscope to the study of metals and established the close analogy which exists between the internal structure of metals and of rocks. Sorby's pioneer work, however, remained neglected for a long time, and the microscopic study of metals and alloys was revived independently in Germany by Martens (A. Martens, Zeitsch. Ver. deut. Ing. 1878, 22, 11) and in France by Osmond (F. Osmond and J. Werth, Compt. rend. 1885, 100, 450). Since then the subject has developed rapidly, and now numbers many enthusiastic workers, among whom may be mentioned in England the late Roberts-Austen, Arnold and Stead; in France Osmond, Le Chatelier, Charpy, and Guillet; and in Germany Heyn, Wust, Friedrich, and Tammann.

The metallographic study of metals and alloys is carried out by both microscopical and physical means, the most important of the latter being the thermal or pyrometric study of the behaviour of these bodies on heating and cooling. Other physical methods, such as measurements of thermal expansion, electrical resistance, solution potential, and many other quantities have also been employed. The pyrometric method is, however, at present far the most fruitful and important, and in the present article attention will be almost entirely confined to this one among the physical methods just referred to. In the majority of metallographic researches the pyrometer and the microscope are practically the only instruments used.

The pyrometric study of metals and alloys consists in observing the phenomena which occur in the heating or cooling of the substance between the ordinary or even an artificially lowered temperature, and a high temperature at which the metal or alloy is completely molten. The phenomena in question arise from the fact that when the substance undergoes either a change of state, an allotropic or polymorphic transformation, or a chemical reaction, these changes are almost universally accompanied by an absorption or an evolution of heat. A familiar example is found in the freezing of water to form ice, a process which is accompanied by the evolution of a very large amount of heat, viz. the latent heat of fusion of the water. If the cooling process of a body liable to such changes is followed with a suitable instrument for measuring temperatures, and the rate of cooling be observed it is found that the occurrence of a heat-evolution at any stage of the cooling process results in a retardation, and sometimes even in an entire cessation of the cooling process—the heat evolved by the transformation of the substance for a time balances the loss of heat due to radiation, condition, &c., and keeps the temperature stationary. For this reason the temperatures at which such changes occur are frequently referred to as 'arrest-points' in the cooling (or heating) 'curves' of the body in question. In the case of metals, these curves are obtained by means of a pyrometer, and generally some form of time-observation which enables the observer to record the rate of cooling over the whole range of temperatures involved. Such observations are most simply represented by plotting them in a curve having the temperature of the metal as ordinate and the time as abscissa, such a curve being known as a 'time-temperature' cooling (or heating) curve; on such a curve the arrest-points are shown as more or less marked flattenings of the curve (Fig. 1). If it is desired to plot such a curve on a large scale—and in practice the temperature range involved may be as much as 1000°—this mode of plotting is found cumbersome, and it is preferable to plot the observations in the form of an 'inverse rate' curve. The ordinates of this curve are again the temperatures of the metal, but the abscissæ are the time-intervals occupied by each successive decrement (or increment) of the temperature of the metal. Thus, during the steady cooling preceding the commencement of solidification, each fall in temperature of 3° might occupy, for example, 12 seconds; then the 3° interval including the commencement of freezing might occupy a time of 120 seconds, the next following fall of 3° might occupy 40 seconds, and the following one as little as 10 seconds; in the inverse-rate curve these observed intervals would be plotted against the mean temperature of each 3° interval. In these curves, uniform rates of cooling are represented by vertical lines, while arrest-points appear in the form of more or less sharp peaks, whose areas approximately represent the quantity of heat evolved by the transformation in question (W. Rosenhain, Observations on Recalescence Curves, Proc Phys. Soc. London, 1908, 21, 180; *see* Fig. 2). Both types of curves represent observations of time and temperature; in another method of working, the temperature of a uniformly cooling body, such as a piece of pure platinum or porcelain, is used as one of the elements of the curve. Against the actual temperature of the cooling piece of metal is plotted the difference between its temperature and that of the neutral comparison body just mentioned; this method—known as the 'differential' or difference method of Roberts-Austen—has the advantage of extreme delicacy, but it is somewhat more laborious and requires more skill on the part of the observer in manipulating the apparatus, while it is also limited to the observation of heat-evolutions occurring at temperatures at which the metal in question remains solid. For all these methods of taking cooling or heating curves, the temperature observations are usually made by means of a thermo-couple whose E.M.F. is measured in some convenient way. The most widespread method of making this measurement is by reading the deflection of a galvanometer, usually of the moving-coil type, but this method has serious disadvantages, and for cases where any considerable accuracy is required the electro-motive force of the couple should be measured accurately by means of some suitable form of potentiometer (W. Rosenhain, The Metallographic Investigation of Alloys, Journ. Inst. Metals, 1909, i. 200; Observations on Recalescence Curves, Proc. Phys. Soc. London, 1908, 21, 180). The neglect of this condition has rendered a large amount of metallographic investigation unreliable.

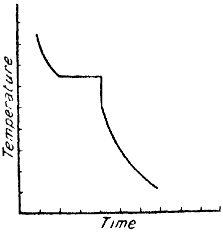


FIG. 1.

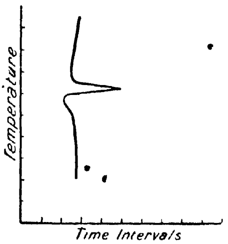


FIG. 2.

Recently, important improvements have been introduced in the methods of taking thermal curves of metals and alloys. So long as the specimens under observation were allowed to follow the 'natural' behaviour of the furnace during heating and cooling, the rate of change of temperature was always much more rapid at the lower end of the temperature scale during heating and at the upper end during cooling, simply because a furnace rises most rapidly in temperature when heating first begins and cools most rapidly while it is still very hot, *i.e.* when cooling commences. This large variation in the rates of heating and cooling within the course of a single curve results in several disadvantages. First, since the maximum rate of heating or cooling must not become excessively rapid, the lower rates which occur at the opposite ends of the curves becomes excessively slow, so that the total time occupied in taking the curve is much prolonged. Further, heat-evolutions or absorptions observed in those parts of the curves taken at a very slow rate are not readily comparable with those observed while the specimen is being heated or cooled at a more normal rate. One way of overcoming this difficulty consists in devising a furnace which can be heated and cooled at a uniform rate throughout the range of temperature required. This can be done by electrical means, but involves the use of a type of furnace which is thermally very inefficient, since the total heat-capacity of the furnace must be kept low if its temperature is to follow the rate of electrical energy supply without material regard to the ordinary laws of cooling. The method has, however, been very successfully employed by Burgess and Crowe at the Bureau of Standards in Washington (Burgess and Crowe, Bulletin, Amer. Inst. Mining Eng. 1913, 2537–2591; also Scientific Papers, No. 213, U.S.A. Bureau of Standards, 1914). Another method, which has been worked out and adopted at the National Physical Laboratory, avoids any attempt to control the rate of cooling or heating of a furnace, but utilises a furnace consisting of a long tube which is kept hot at one end and cold at the other; the specimen under observation is moved along this tube by mechanical means at a constant rate and is thus heated or cooled at a correspondingly constant rate. These 'gradient furnaces' have given very good results, and they have the considerable advantage that the rate of heating or cooling can be varied at will so as to suit different purposes (Rosenhain, Some Appliances for Metallographic Research, Journ. Inst. Metals, 1915, [xiii.] I, 160–192).

Much attention has also been given to methods of recording thermal curves. In some respects, photographic records are advantageous, particularly on the ground that they are autographic and to some extent free from personal error; they have, however, the grave objection that the scale which can be employed is necessarily limited to relatively small dimensions so that no great degree of sensitiveness can be reached. For that reason, for the most accurate and delicate work, photographic methods are now largely discarded, and observations are taken by eye and recorded by means of a chronograph. If this is done by means of an ordinary drum or tape chronograph, the subsequent labour of reading off and plotting the observations becomes very great and a certain possibility of error arises. Both these difficulties have been overcome by a special type of 'Plotting Chronograph' (*see* Rosenhain, Some Appliances for Metallographic Research, as above). This instrument, from the tapping of a key by the observer, plots directly and automatically the inverse-rate thermal curve on a very open scale and in a manner which largely eliminates the risk of undetected errors or observation.

The cooling-curves of metals and alloys, taken from a temperature at which the metal is liquid downwards, always show as the highest arrest point the initial 'freezing-point' of the metal; below this temperature, at which the liquid metal first begins to deposit solid crystals, the cooling-curves may show from one up to four or five further arrest-points, even in simple alloys containing two metals only. In studying such a 'binary' system of alloys, the arrest-points on the cooling-curve of each alloy are generally plotted as points on a diagram in which the concentration of the alloy is used as abscissa and the temperatures as ordinates, the result being a temperature-concentration diagram. If properly completed in such a manner as to indicate all the conditions in which alloys of the two metals can exist in equilibrium at all possible temperatures and concentrations, this diagram is termed the 'equilibrium diagram' of the binary system in question. As a rule, however, the mere plotting of observed arrest-points in the cooling-curves of a series of alloys is not enough to allow such a diagram to be drawn, the evidence of the microscope and of other physical methods being often required to allow of the correct interpretation of the arrest-points observed. The first and simplest line of such an equilibrium diagram is that known as the 'liquidus'; this is the boundary of the region in which the alloys are completely liquid; immediately below the 'liquidus' the alloys in general consist of a mixture of liquid with solid crystals, although in some cases the range of temperature over which such a mixture occurs is very short—in pure bodies, consisting entirely of one chemical entity (pure element or pure compound) the whole process of solidification occurs at a single definite temperature and no region of mixed solid and liquid exists. The liquidus line of the equilibrium diagram can, as a rule, be drawn definitely from pyrometric observations alone, although exceptions occur in the case of pairs of metals possessing either limited miscibility in the liquid state or where the formation of a definite compound takes place slowly in the liquid metal. In other cases, small breaks of continuity in the liquidus curve cannot be definitely located by pyrometric observations alone.

The process of solidification which follows, in any given alloy, upon the commencement of freezing at the temperature of the 'liquidus' curve depends, in the first place, upon the position of the alloy in the binary system to which it belongs and also upon the type which that system follows. The type depends again upon the manner in which the two component metals undergo mutual mixture, solution, combination, or separation during freezing and melting. A large number of these types can be distinguished, but only the most important can be mentioned here. The first and simplest type are those alloys in which the two metals, when they have reached their final equilibrium in the solid state, retain the condition of intimate mixture in which they existed in the liquid state at a higher temperature. In the language of metallography, two such metals form an unbroken series of solid solutions. In their final condition such alloys resemble pure metals in being built up of an aggregate of crystals which are all alike in composition and properties. In the cooling and freezing process, however, the alloys of such a series differ markedly from pure metals in showing at times a very wide range of temperature over which the freezing process is distributed. The equilibrium diagram of such a system of alloys is shown in Fig. 3, the line ACB representing the liquidus or line of commencing freezing, and ASB representing the line of complete solidification or 'solidus.' At temperatures lying between these two lines the alloys consist of a definite proportion of solid crystals in equilibrium with liquid alloy, but it is important to notice that the compositions of the crystals and of the liquid in equilibrium with them are not identical.

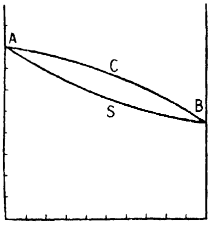


FIG. 3.

The opposite extreme to the type of alloys just described is found in those groups where the component metals are completely, or almost completely, immiscible in the solid state. A typical equilibrium diagram of this type is shown in Fig. 4, where the liquidus curve is represented by the lines ACB, forming a more or less deep V; the addition of the metal A to the metal B lowers the temperature of initial freezing, and this lowering is continued with increasing additions of B. Similarly successive additions of A lower the initial freezing temperature of B until a concentration is attained where the two branches of the liquidus curve meet at the point C, which represents the freezing-point of the most fusible alloy of the series. This alloy, both in the free state and when it occurs as a constituent of alloys of different composition, is known as the 'eutectic' alloy of the series, or more briefly as 'the eutectic' (Guthrie, Phil. Mag. 1884, [v.] 17, 462). This eutectic alloy shares with the pure metals and with pure inter-metallic compounds the property of undergoing complete solidification at one temperature instead of showing a 'freezing range.' The solidification of any alloy of intermediate composition, such as that represented by the line

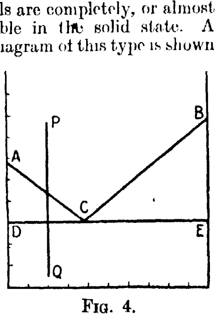


FIG. 4.

PQ, may be described as follows: when the cooling alloy reaches the temperature at which the lines PQ and AC intersect, solid crystals begin to separate, but these are crystals of the metal A. As a result of this separation, the residual liquid metal or 'mother liquor' becomes enriched in B; the residual liquid is now, in fact, an alloy lying further to the right than the line PQ. As the temperature falls, the temperature of initial freezing of this richer alloy is reached and a further quantity of solid A is separated, again increasing the concentration of B in the liquid. This process is continued until the concentration of the point C, and its temperature, are simultaneously reached. At that point the residual liquid has the composition of the eutectic alloy and solidifies as such. The alloy thus becomes completely solid on reaching the temperature of the line DE, which is usually called the eutectic line—this line (CE) is, therefore, in this case, the 'solidus' of the system, since it forms the boundary of the region of completely solid alloys. An alloy such as PQ, at all temperatures below that of DE consists of an agglomerate of crystals of the metal A embedded in a matrix of the eutectic alloy; if the composition of the alloy is such that the line PQ lies close to A, then the crystals of A in the solid alloy will be large and numerous, and little eutectic will be present, while, as the point C is approached, the proportion of eutectic increases. On the other side of C, the alloys consist of crystals of B embedded in the eutectic, and these crystals increase in amount as we move from C to B. Actual examples of binary alloys strictly following this simple type are rare, if indeed they exist at all; so far as at present known the alloys of lead and antimony approximate closely to this type (Antimony-Lead, Gautier, Recherches sur la fusibilité des alliages métalliques, Bulletin de la Soc. d'Encouragement, 1896; Gold-Thallium, Levin, Zeitsch. anorg. Chem. 1905, 45, 31). The great majority of alloys, however, belong to a type which is intermediate between the two extremes which have just been described; this intermediate type consists of alloys in which the two component metals are mutually soluble in the solid state to a limited extent. The typical equilibrium diagram of this class is given in Fig. 5 The liquidus is very similar to that of type II., a eutectic point being again evident at C, but the eutectic line DE no longer crosses the whole width of the diagram. Alloys from O and F and from H to G behave as regards solidification exactly like alloys of type I., forming homogeneous crystalline aggregates which consist of only a single constituent. Alloys from F to G, however, behave like members of type II., but with the difference that the substance which commences to crystallise when these alloys reach the temperature of the line AC is not pure A, but a solid solution of B in A, or, if the alloy lies to the right of C, the crystals consist of a solid solution of A in B.

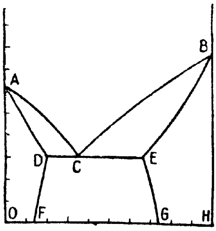


Fig. 5.

A considerable number of further types of binary series of alloys can be distinguished, but it is not possible to deal with these fully here. The only other class which need be mentioned are those in which a definite inter-metallic compound is formed. A typical equilibrium diagram of such a series is shown in Fig. 6, where the liquidus curve ACPDB shows a maximum (P) and two minima or eutectic points, C and D. The occurrence of a maximum in the curve of initial freezing, such as that shown at P, is a definite indication of the existence of an intermetallic compound, although the presence of such compounds is not always shown in this way. The simplest way of regarding an equilibrium diagram of the type shown in Fig. 6, is to suppose it divided into two separate diagrams by the vertical line through P, the one half being thus a diagram of the alloys of A with the compound metal P, and the other half representing the alloys of B with P. In the diagram as drawn, the left-hand half then becomes a diagram of type II., while the right-hand half falls under type III. It should be mentioned, however, that in actual alloys the formation of the compound P may not take place quite completely, and the alloys may in reality contain some free B as well as A and P—the system thus becomes practically one of three components, to which reference is made below.

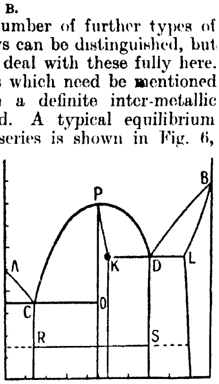


Fig. 6.

Equilibrium diagrams frequently contain lines other than those forming parts of the 'liquidus' and 'solidus' curves; these lines represent the occurrence of transformations or chemical reactions within the metal, frequently at temperatures well below those at which the alloys are completely solid. These changes are represented on the cooling curves by heat evolutions or absorptions, which are sometimes so faint as to escape detection by any but the most sensitive instruments, while in other cases they rival the freezing-point in intensity. These heat evolutions may represent either:

(1) An allotropic change in a pure metal or in the pure metal forming the basis of a solid solution or existing in the form of crystals in a eutectiferous alloy.

(2) A polymorphic change in an inter-metallic compound.

(3) A chemical reaction resulting in the formation or the decomposition of a compound or of a solid solution.

Two or more of these changes may occur together. An example of such a change is indicated in an imaginary case by the line RS in Fig. 6, which is supposed to represent the decomposition of the compound P. It will be seen that the line extends over the whole range of composition in which the compound P can exist, either as free crystals or as a constituent of the eutectics in which it occurs. As a rule, however, it is difficult, and sometimes impossible, to find any evidence—either pyrometric or otherwise—for the occurrence of such changes in alloys where the compound in question exists only as a constituent of a eutectic; the line of transformation is therefore shown as a full line only between the points R and S, where the compound exists in the form of primary crystals, and as a dotted line over the rest of the range of its existence. The interpretation of such a line of arrest-points in an equilibrium diagram will, as a rule, be based principally upon microscopic evidence, and this also applies to several of the other facts tacitly implied in such a diagram as that of Fig. 6; but before passing on to consider the microscopic study of alloys, certain other lines of pyrometric evidence must be mentioned.

The most important of these is the determination of the end-points of a series of arrest-points, and of the point of maximum intensity of such a series. The first of these is important for fixing the position of such points as D and E in Fig. 5, and O, K, and L in Fig. 6. Points D, E, K, and L serve to fix the limits of solid solubility of the metals and compounds in one another, while the point O assists in determining the exact composition of the compound P, since the maximum in the liquidus curve is not always very sharply marked. Probably the best method of determining the end-point of such a series of arrests consists in observing, by means of the most delicate pyrometric apparatus available, large samples of the alloys cooling at a slow rate, but it is also necessary in such cases to secure the complete equilibrium of the alloy at a temperature just above that of the arrest to be observed. For this purpose it is necessary, in some cases, to maintain the specimens of alloy at a definite, more or less high, temperature for prolonged periods—sometimes up to several weeks—and then to take the observations of cooling without having allowed the specimens to cool down intermediately (Rosenhain and Archbutt, Aluminium-Zinc Alloys, Phil. Trans. 1911, A, 211). The exact end-point found, however, will always lie a little short of the true end-point. For this reason a method of extrapolation is often employed. If the quantities of heat evolved at such a series of arrest-points were measured, the measurements being reduced to quantities of heat per gramme of alloy, then a curve could be plotted with concentration as abscissæ and quantities of heat evolved as ordinates. Provided that the measurements were strictly accurate, such a curve would simply be a straight line running from the concentration at which the heat-evolution was largest down to the two end-points of the series; even if not observed very close to these end-points, the line could be continued until it cut the axis, and this intersection would indicate the true end-point of the heat-evolutions. In practice this method is frequently applied, especially by Tammann and his school (Tammann, Zeitsch. anorg. Chem. 1903, 37, 303), both for the determination of end-points and of maxima of heat-evolutions; but unfortunately it is not possible to make the measurements of the quantities of heat evolved with any great degree of accuracy. The determination of the duration of the arrest itself or of the area of the peak of the inverse-rate cooling curves is usually employed, and it has been shown that this is only a rough approximation; the variation of specific heat with concentration of the alloys also affects the shape of these intensity curves, so that very great care is required in employing this method, which has more than once led to erroneous results (W. Rosenhain, The Metallographic Investigation of Alloys. Journ. Inst. Metals, 1909, i. 200; Observations on Recalescence Curves, Proc. Phys. Soc. London, 1908, 21, 180; Rosenhain and Tucker, Lead-Tin Alloys, Phil. Trans. 1908, A, 89; Rosenhain and Archbutt, Aluminium-Zinc Alloys, Phil. Trans. 1911, A, 211).

The above account of the pyrometric study of alloys and its diagrammatic representation has so far dealt only with alloys consisting of two component metals; in practice, however, alloys frequently contain three or more metals. Unfortunately the difficulty of making a complete metallographic study of a system of alloys increases very rapidly with the number of component metals; for fifty determinations required for the elucidation of a binary system of alloys, 1250 would be required for a system of three metals, while no attempt at the complete systematic study of a quaternary system (of four metals) has yet been made, but for corresponding completeness over 30,000 determinations would be needed In the case of a ternary system (of three metals) it is still possible to employ graphic representation. The concentrations of a system of ternary alloys may be plotted in the form of an equilateral triangle, each corner representing one of the pure component metals; each side of the triangle then represents one of the three limiting binary systems, while the position of any point within the triangle represents the composition of an alloy of a ternary system, on the principle of trilinear co-ordinates. Upon this equilateral triangle as a base, the 'equilibrium diagram' can be erected as a three-dimensional model, ordinates representing temperature being erected upon each point of the area of the triangle. A few such equilibrium models of ternary systems have been more or less completely determined (Lead-Tin-Bismuth, G. Charpy, Compt. rend. 1898, 126, 1569; E. S. Shepherd, J. Phys. Chem. 1902, 6, 519; Lead - Cadmium - Mercury, E. Janecke, Zeitsch. physikal. Chem. 1901, 60, 399; Magnesium - Lead - Tin, A von Vegesack, Zeitsch. anorg. Chem. 1901, 54, 367; Aluminium-Copper Manganese, Rosenhain and Lantsberry, Ninth Report to the Alloys Research Committee, Proc. Inst. Mech. Eng. 1910), but the field is still largely unexplored. It is interesting to note, however, that very few tri-metallic compounds have yet been discovered

The microscopic study of metals is always carried out by looking at suitably prepared surfaces illuminated by reflected light; the thin sections employed in petrography cannot be used in the case of metals, as these are too opaque for such a purpose. The preparation of a suitable surface for examination by reflected light consists in three distinct processes, viz. the cutting and grinding of a small flat area, the fine-polishing of this surface in order to remove physical irregularities, and the treatment of this polished surface in such a manner as to indicate the nature of the structure of the metal beneath. The cutting and grinding process, in the first place, consists in preparing an area, as nearly flat as possible, which may range in size from a few square millimetres to several square centimetres but the difficulty of the subsequent operations increases rapidly with the area to be treated, so that it is preferable to examine several small specimens rather than one very large one. The initial rough cutting and grinding is followed by some process of fine grinding, generally by the use of carefully graded abrasives, each stage reducing the depth of the scratches left on the surface.

The grinding operation is followed by that of fine-polishing. The purpose of this process differs essentially from that of the ordinary polishing process, the object of which is solely the production of the most brilliant surface; in most ordinary polishing processes this is largely accomplished by a species of 'burnishing' action, in which there is much surface flow of the metal, the previously existing scratches being largely 'smeared over' and filled up. For metallographic purposes this action should be avoided as far as possible, since scratches or holes thus hidden immediately become conspicuous under subsequent treatment (etching). It follows that for this work the entire processes of cutting, grinding, and polishing, should be conducted as gently as possible, particularly in the case of the softer metals. For polishing purposes a material which acts as an exceedingly fine abrasive is indeed more preferable to one which, though more rapid in action, tends to cause flow. The polishing materials most widely used consist of the oxides of such metals as aluminium, magnesium, and iron, alumina being probably the best.

A perfectly polished metallic specimen shows, under the microscope, a featureless surface, which will appear either uniformly bright or uniformly dark, according as the light falling upon it is or is not reflected into the objective of the microscope. In order to obtain a sectional view of the structure of the metal it is necessary to employ some method of 'etching.' As a rule, this consists in exposing the specimen to the action of some reagent, such as a weak acid, which gradually dissolves the metal. It is found that this solution does not take place uniformly over the surface of the metal, and that, in fact, it differentiates clearly and consistently the various constituents of metals and alloys. In the case of pure metals and of certain alloys which consist of a single constituent or phase, the etching agent cannot, of course, act by differentiating two or more distinct constituents; but in that case a differentiation occurs between the different crystals of the same constituent, the rate of attack being apparently dependent upon the orientation of the particular section of the crystal exposed to the solvent. Such a 'homogeneous' metal consists, in fact, of an aggregate of minute crystals which have grown together in such a manner that the boundary of each crystal is determined not by the natural symmetrical surfaces commonly associated with the term 'crystal,' but by the surfaces of mutual interference of adjacent crystals—each crystal has grown until checked by meeting its neighbour. In section such a structure exhibits a network of roughly polygonal areas, and the etching reagents employed in metallography attack these various areas at different rates, thus producing both differences of level and varieties of surface texture which readily reveal the arrangement of the constituent crystals. In the case of alloys possessing a duplex or more complex structure, although each of the constituents is still built up of such aggregated crystals, the differences of solubility between the various constituents are very much greater than those between adjacent crystals of the same constituent. Consequently the resulting surface pattern generally shows all those areas which represent sections of crystals of one of the constituents as comparatively deeply etched or eroded, while those corresponding to the other constituent remain practically untouched. In duplex alloys, therefore, etching reveals the distribution of the constituents rather than the crystal structure of any of them.

The specimens of metal thus prepared can be examined by means of almost any good ordinary microscope if it is provided with certain special accessories, but for the greatest convenience and for more refined purposes it is desirable to employ one or other of the specially designed 'metallurgical' microscopes. Two general types of such instruments have been evolved for this special purpose. In the one type, which is generally used by British workers, the ordinary arrangement of the microscope is adhered to, but the stage is provided with a focussing movement, while the body-tube is provided with one of the devices known as 'vertical illuminators.' In the most highly specialised instrument of this kind (Rosenhain, On an Improved Form of Metallurgical Microscope, Journ. R. Microscopical Soc. 1906) the body-tube is entirely fixed to the limb and all the focussing, both coarse and fine, is done by movements of the stage; further, the illuminating arrangements are made integral with the main tube of the instrument, while in other microscopes they are removable and are only screwed on at the lower end of the tube. The function of the 'vertical illuminator' is simply that of sending a beam of light down the tube of the microscope in such a way as to fall upon the back lens of the objective, and then, after being concentrated by the objective, to fall upon the specimen and to illuminate the portion of the surface which is under examination. Such a vertical illuminator consists essentially of a reflector, which may be a thin disc of glass or an opaque reflector or a totally reflecting prism so placed as to cover one-half or less than one-half of the aperture of the objective. The path of the light-rays in both cases is shown diagrammatically in Fig. 7. It will be seen that under this mode of illumination the light falls upon the surface of the specimen in a direction more or less parallel to the optical axis of the microscope, and as this is sometimes placed vertically, this mode of illumination has received the name of 'vertical illumination,' although 'normal illumination' is a more rational term, since the light remains normal to the surface of the specimen whatever the position of the microscope. Under this mode of illumination it is evident that flat, bright surfaces will appear light, while sloping surfaces, or areas rendered rough so as to scatter the light which falls upon them, will appear dark—since the light reflected from such regions will be more or less completely thrown outside the aperture of the objective of the microscope. With lenses of moderate power, which leave a certain amount of space between the lens and the specimen, the surface under examination may be illuminated directly by a beam of light falling obliquely upon the surface of the specimen, in the manner indicated in Fig. 8. With such lighting, plane polished surfaces will appear dark, while those with a suitable slope and those roughened so as to scatter the incident light, will appear more or less bright; the consequence is that in many respects the image as seen by 'oblique illumination' bears to that seen by 'normal illumination' a relationship like that of a photographic negative to its positive. Oblique illumination, however, is much more searching, particularly as regards minute holes and scratches, while it also tends to reveal the natural colours of the various constituents much more definitely than normal light. On the other hand, its application is generally limited to magnifications not much greater than 200 diameters, while normal illumination is readily employed with the highest powers of the microscope.

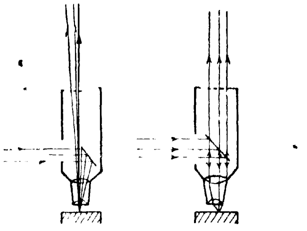


Fig. 7.

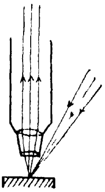


Fig. 8.

The use of the vertical illuminator, whether as a permanent or a more or less temporary attachment to the microscope, entails a special arrangement of the source of light. Whether this be an ordinary lamp or some more or less elaborate optical system, it must be so placed that the light coming from it enters the aperture of the illuminator at the desired angle. This requires a definite relative position of the source of light and the illuminator itself. In any ordinary microscope where focussing is done by moving the tube of the instrument, the position of the illuminator will vary with every adjustment of the focus, and this would entail corresponding re-adjustment of the source of light. By using a focussing stage and leaving the body-tube with the illuminator attached to it in a fixed position, this difficulty is overcome, and this arrangement is the essential feature of the majority of metallurgical microscopes. For certain purposes, of course, special provision for taking large and heavy specimens, for complete rotation of the specimens, and for other special requirements is desirable and can be obtained.

The second type of metallurgical microscope originated with H. le Chatelier (Le Chatelier, Étude des Alliages, 1901, 421), and its use is widely extended in France and Germany. The observation tube of this instrument is horizontal, and directly in line with a tube carrying condensing lenses through which light from a suitable source is concentrated upon the specimen. The stage of this instrument is a table provided with a small hole, and the specimen is placed over this hole, polished face downwards. The objective of the microscope faces upwards towards the specimen, and the incoming light as well as the rays forming the image are turned off at right angles by means of two totally reflecting prisms. In its most recent forms this instrument presents many points of great convenience, but it also possesses certain very marked limitations and disadvantages from which the more ordinary type of microscope is free.

The observations of the structures of metals and alloys made by such microscopes are readily recorded by means of photography. If the beam of light employed for illuminating the specimens is made sufficiently powerful, and particularly if the ordinary eyepiece of the microscope is replaced by one of the well-known 'projection eyepieces' now available, the image of the surface under examination can be projected upon a screen, and this image can be made large enough and bright enough to be visible even to an audience of moderate size. Instead of projecting the image upon a large screen it can equally well be focussed upon the ground glass of a suitably placed camera, and there photographed in the ordinary manner. The manipulation requires some experience and skill, particularly when very high magnifications are attempted, but in principle it does not differ materially from ordinary photography, except that the microscope with its system of lenses is used in place of the ordinary camera lens.

The typical micro-structures met with in metals and alloys may now be briefly considered. We have already indicated that a pure metal is an aggregate of minute crystals whose sections, in the form of irregular, more or less polygonal areas, are revealed by etching a polished surface. In such metals as cast lead or tin the crystals are often very large, and can be seen without the aid of the microscope, but in iron and copper they are usually very small and require magnifications ranging from 100 to 400 diameters to be readily observed. Seen under normal illumination, the crystals of iron appear as illustrated in Fig. 9, Plate I.; the same field of view seen under oblique light is shown in Fig. 10, Plate I. The appearance there seen arises from the fact that the etched surface of each crystal is covered with a number of minute facets all similarly oriented over the whole area of the same crystal, but differing in orientation from one crystal to the next. Oblique light falling on a surface thus constituted picks out those areas where the facets are so placed as to reflect the light into the microscope, and these areas accordingly appear bright, while others, situated unfavourably, appear more or less dark. A rotation of the specimen on the stage of the microscope alters these relative positions, and different crystals appear bright in turn.

The description of the typical structure of a pure metal which has just been given applies

PLATE I.

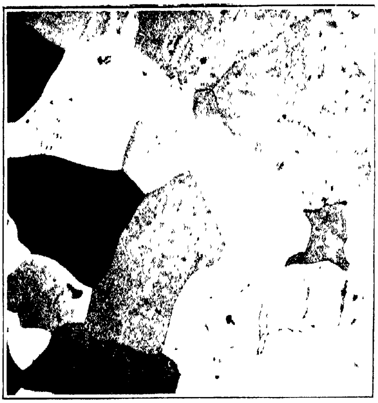


FIG. 9.

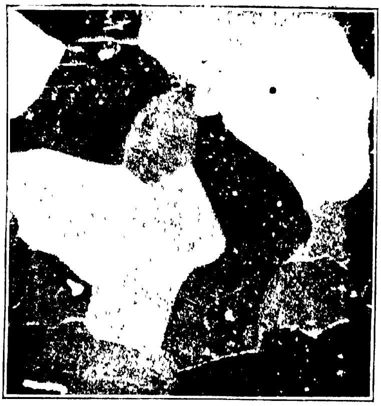


FIG. 10.

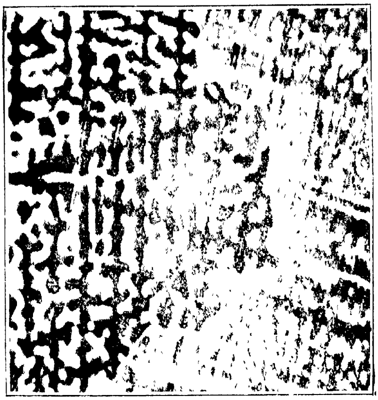


FIG. 11.

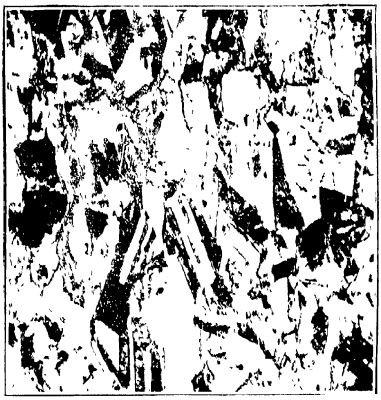


FIG. 12.

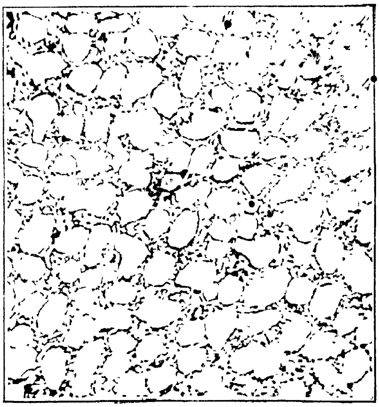


FIG. 13.

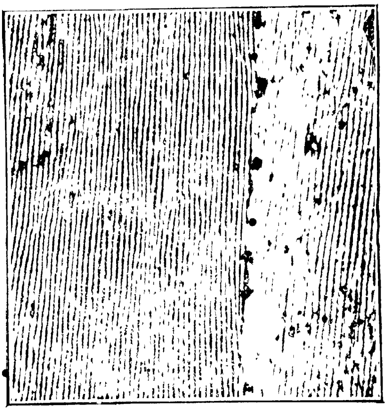


FIG. 14.

[*To face* p. 28

equally to the structure of those alloys which consist either entirely of a definite intermetallic compound in a state of purity, or of a homogeneous 'solid solution.' The term 'solid solution'—sometimes called 'mixed crystals'—implies a state of mutual admixture or solution existing in the solid state which is as intimate as the condition of liquid solutions; probably the best interpretation of the conception is to regard the crystals of a solid solution as being built up of molecules of both the solvent and the solute indiscriminately. Where the two metals are completely isomorphous, these composite crystals may be built up of two kinds of molecules indiscriminately in any proportion, and we then have a series of alloys consisting of solid solutions only; in other cases the number of molecules of the solute which can be incorporated in the crystals of the solvent is limited, and in that case there is a limit to the 'solid solubility' of the two metals. While the final condition of a solid solution is thus simply that of an aggregate of homogeneous crystals resembling in appearance and character the structure of a pure metal, this final condition is not at once arrived at during the solidification of such an alloy. The central part of each individual crystal of such a solid solution when first formed contains considerably less of the solute than the liquid alloy from which it is being deposited, and as solidification proceeds this core of relatively dilute solid solution is surrounded by successive layers of more and more concentrated solid solution. Ideally the concentrations of these layers should be continually equalised by diffusion of the solute from the more concentrated to the less concentrated regions, but this is a slow process, and generally remains incomplete during the ordinary cooling of an alloy from fusion. Samples of alloys consisting of a single solid solution when taken from castings which have not been subjected to prolonged annealing, therefore always show traces of the original 'cores' within the polyhedral crystals. An example of this kind in the case of cast brass is shown in Fig. 11, Plate I. When this alloy has been reheated and subjected to such a process as rolling into bars or rods, these 'cores' are obliterated, and a homogeneous polyhedral structure is then found, such as that illustrated in Fig. 12, Plate I.

We may now consider the micro-structure of such an alloy as that represented by the line PQ in Fig. 4. In accordance with the nature of the freezing process of such an alloy, which has already been described, the microscope shows that it consists of two very distinct constituents; as a rule one of these, which represents the crystals of the pure metal A, remains practically unaffected by the etching reagent, while the other, which represents the eutectic, is more or less eroded and darkened. The relation between the two constituents is readily followed if a series of alloys are considered, commencing with one very rich in A and gradually increasing the concentration of B. At first the micro-structure closely resembles that of a pure metal, but the boundaries between adjacent crystals are seen to be thicker than the fine lines observed in pure metals. With a very slightly higher concentration of B the presence of a dark-etching constituent between the crystals of A becomes evident, and as the concentration of B increases the proportion of this dark-etching constituent (the eutectic) increases, while the crystals of A become mere islands. Ultimately, as the concentration of the point C is reached these islands of A disappear entirely, and the whole field is occupied by the eutectic. An example of such a eutectiferous alloy lying midway between the pure metal and the pure eutectic is shown in Fig. 13, Plate I., while the typical structure of a pure eutectic is shown, under much higher magnification, in Fig. 14, Plate I. It will be seen that the 'dark etching' eutectic is not uniformly etched, but itself exhibits a duplex structure, which is frequently found in these bodies, although it is not one of their essential characters. The eutectic, as it crystallises from the residual mother-liquor along the eutectic lines, such as DE, Fig. 4, is really the product of the simultaneous crystallisation of both the constituents, and we thus generally find it with a laminated structure consisting of alternating layers of the two constituents. It was formerly thought that these were simply minute independent crystals deposited side by side, but later research has shown that most eutectics crystallise in the form of the predominating constituent, the crystals of the one metal being forced into the interstices of the other, the whole arrangement frequently adopting the spherulitic form (Rosenhain and Tucker, Lead-Tin Alloys, Phil. Trans. 1908, A, 89).

The great majority of alloys exhibit in their micro-structures varieties of the three types illustrated and described above, but in a certain number of cases special structures are met with.

In the course of metallographic investigations it is frequently necessary to adopt special methods for determining the exact temperature at which the solidification of a given alloy is completed. For various reasons it has been found that the best available method of making this determination is by a process of quenching small pieces of the alloy from a series of suitably chosen temperatures. By the micro-structure of the quenched specimen it is then possible to determine whether the alloy contained any liquid at the moment of quenching. The rationale of this process lies in the fact that while that part of the alloy which was solid at the instant of quenching had solidified slowly, and had, therefore, been allowed to form relatively large crystals, any liquid metal present when the specimen was suddenly cooled would be forced to solidify very rapidly and would, therefore, form extremely minute crystals. Thus in a series of specimens quenched from successively higher temperatures, it is found that the resulting specimens show the ordinary typical and comparatively large-scale structure of the alloy until the quenching temperature exceeds a certain limit, but that beyond that point small areas of very minute crystals are found. It may then be concluded that the limiting temperature in question is that of the final solidification of the alloy. The first traces of 'liquid' in such specimens appear as minute dots or 'fusion spots,' but with slightly higher temperatures the original solid crystals of the alloy are seen to be embedded in a matrix which had obviously been fluid at the moment of quenching.

When such a quenching process is employed for locating one of the lines of an equilibrium diagram, it is of great importance that the exact temperature of the specimen at the moment of quenching should be accurately known, and that the small specimens should be protected from oxidation as far as possible during the progress of the experiment in order to avoid changes of composition and structure. In all earlier investigations quenching was carried out by heating the specimens in a small furnace, and when the desired temperature had been attained, withdrawing them by means of a rod or wire and quickly throwing them into water or other quenching fluid. More recently an apparatus has been devised (Rosenhain, The Metallurgical and Chemical Laboratories in the National Physical Laboratory, Journ. Iron and Steel Inst. 1908, I.) in which the specimen is heated electrically while contained in an exhausted tube made of fused silica; when the desired temperature has been reached, water is admitted into this exhausted tube through a wide-bore tap, and the powerful stream of water, driven by the pressure of the atmosphere, quenches the specimen, and carries it out of the furnace with it; the quenching is thus carried out very rapidly at an accurately known temperature, and without any exposure to the atmosphere.

Apart from the processes of solidification, a great many metals and alloys undergo transformations which are frequently accompanied by thermal phenomena shown on the cooling-curves, and, as a rule, these transformations are accompanied by more or less striking changes in micro-structures. In the case of pure metals these changes occurring at temperatures below that of solidification are generally regarded as being 'allotropic'; in the case of alloys, however, these transformations or 'inversions' may arise from a variety of causes, such as the formation or decomposition of a compound, an allotropic change in one of the components resulting in the rejection of the other component from solid solution, or the rejection from solid solution of a phase the limit of solubility of which has been reached owing to a variation of solid solubility with temperature. Typical examples of these and similar changes are met with in such systems of alloys as iron-carbon, copper-tin, copper-zinc, copper-aluminium, aluminium-zinc, and others, and some of these will be referred to in connection with the equilibrium diagrams of these systems.

The equilibrium diagrams and general metallography of some of the more important alloys will now be briefly described. Among alloys forming uninterrupted series of solid solutions (type I. above) perhaps the most important are the iron manganese and the copper-nickel series, whilst iron-nickel and copper-manganese probably also belong to this type. The equilibrium diagram of the copper-nickel series is given in Fig. 15, these alloys being important on account of their electrical uses (resistance alloys) and also as forming the basis of such industrially important metals as '*Nickel silver*' and Monel metal. Cupro-nickel is also very extensively used in the production of rifle-bullet envelopes. The diagram is of the simplest type, and the micro-structures met with in the alloys are correspondingly simple—in the cast alloys some core-formation is visible, but in the worked materials, such as sheet or wire, complete homogeneity is attained, the resulting structure being very similar to that of brass (*see* Fig. 12, Plate I.), but usually on a more minute scale.

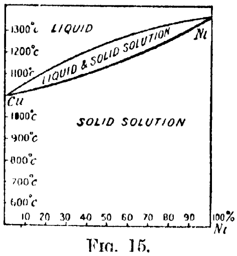


FIG. 15.

A characteristic example of another type of equilibrium diagram is that of the alloys of lead and tin, which are important on account of their use as solder, pewter, &c., and also because they form the basis of important ternary and quaternary alloys such as certain anti-friction alloys and type-metal. The diagram given in Fig. 16 (Rosenhain and Tucker, Lead-Tin Alloys, Phil. Trans. 1908, A, 89) shows the typical **V**-shaped liquidus with a long eutectic line running up to, or very nearly up to, the tin end of the series, but stopping some little distance (at about 18 p.c. of tin) from the lead end. Formerly the line was supposed to run up to the lead end also, but this was an error arising from the fact that these alloys take up their equilibrium condition very slowly, so that alloys cooled from fusion in the ordinary way show eutectic practically up to the lead end; this, however, disappears on prolonged heating of the alloys at a temperature near 170°. Below the solidus this diagram shows a line indicating an inversion occurring in the alloys from 18 to 63 p.c. of tin at a temperature of 150°, but with lower tin-contents the temperature at which this change occurs falls rapidly, and the inversion cannot be traced at all at concentrations of less than 8 p.c. of tin. This inversion is accompanied by a partial rejection of the tin from solid solution, and involves a change of density.

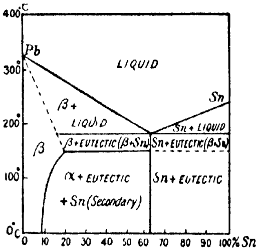


FIG. 16.

As typical of a comparatively simple system exhibiting a maximum in the liquidus corresponding to a definite compound, the alloys of silicon and magnesium may be taken (Vogel, Zeitsch. anorg. Chem. 1909, 61, 46–53). These alloys are of some importance in the case of certain aluminium alloys in which both silicon and magnesium are present. The constitutional diagram of these alloys, as far as it is at present known, is given in Fig. 17. The liquidus has four branches: Si–I. corresponding to the commencement of the deposition of silicon containing but little magnesium in solid solution, I.–II. and II.–III. both corresponding to the deposition of crystals of the compound Mg_2Si, and III.–Mg corresponding to the commencement of crystallisation of magnesium containing only a small amount of silicon in solid solution.

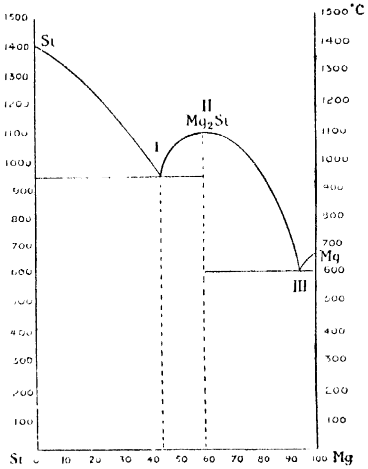


Fig. 17.

The diagram further shows the existence of two distinct and well-defined eutectics, one composed of silicon and the compound Mg_2Si, and the other of magnesium and the compound. The diagram as drawn does not indicate the solubility of any of the three phases in one another, but it is very probable that when the system has been more fully studied, distinct ranges of solubility, resulting in the formation of solid solutions, will be found. In such a system the micro-structures of the alloys correspond very clearly with the indications of the diagram. Thus the alloys corresponding to the branch Mg III. of the liquidus show crystals of magnesium embedded in the Mg-Mg_2Si eutectic; those corresponding to the branch III.–II. show crystals of Mg_2Si embedded in the same eutectic, and correspondingly for the two remaining branches. Alloys of the exact composition of the compound Mg_2Si or, at least, exact within the limits of solid solubility which may exist, exhibit the structure of a simple homogeneous crystalline aggregate. In this connection it is, however, interesting to note that inter-metallic compounds such as the body Mg_2Si are almost always exceedingly brittle bodies, even when their constituent metals are soft and ductile. Compounds of copper with such metals as tin and aluminium form striking examples of this fact. It follows that in those binary alloys where a definite intermetallic compound is formed, over a considerable range of composition on either side of this compound the alloys are usually so brittle that they cannot be used for any technical purpose; this removes the greater part of the ranges of most binary systems from all practical usefulness, and in fact it is found that industrially useful alloys rarely contain much more than 15 p.c. of substances other than the predominating metal. The only real exceptions to this rule are to be found in the alloys of zinc with such metals as copper and aluminium; apparently the addition of zinc can be pushed much further without producing serious brittleness than is the case with any other metal, and industrially useful alloys containing over 40 p.c. of zinc are well known. The alloys of lead and tin furnish another example, but in their case practical utility does not depend upon mechanical strength: similarly in certain anti-friction or bearing metals large proportions of added elements are sometimes employed, but these alloys are intended to meet special requirements and a considerable degree of brittleness is permissible.

Probably the most widely used of all non-ferrous alloys are those of copper and zinc, which include the whole series of 'brasses,' although in many industrial varieties of brass other metals besides copper and zinc are met with in varying proportions. It should perhaps be mentioned here that a considerable degree of confusion has arisen in connection with the terms 'brass' and 'bronze' which have been used very loosely or even indiscriminately. The matter has, however, been dealt with by a Nomenclature Committee of the Institute of Metals, in whose Report (Journ. Inst. Metals, 1914, i. 45-55) these terms have been authoritatively defined. 'Brass,' used alone, denotes an alloy of zinc and copper in which copper preponderates; 'bronze' similarly denotes an alloy of tin and copper in which copper preponderates, while the presence of a third metal in the alloy is to be indicated by a prefix such as 'tin-brass' or 'phosphor-bronze.'

The equilibrium diagram of the zinc-copper alloys, as worked out by Shepherd (Copper-Zinc Alloys, E. S. Shepherd, J. Phys. Chem. 1904, 8, 421), and modified in accordance with the work of Carpenter and Edwards (Copper-Zinc Alloys, H. C. H. Carpenter and C. A. Edwards, Journ. Inst. Metals, v. 1911), is given in Fig. 18. In this diagram each of the six Greek letters indicates a definite phase; according to Shepherd these are all solid solutions, but it appears probable that each of these solid solutions owes its separate existence to some definite compound associated with it—there is some evidence for the existence of the two compounds Cu_2Zn and Cu_2Zn_3. It will not be necessary to discuss the whole of this diagram in detail, since the industrially important alloys consist either of pure α, or a mixture of α and β, and in special cases of either pure β or of β with a little γ; in accordance

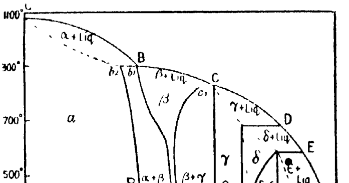


Fig. 18.

with what has been stated above in general terms, the β phase is decidedly harder and stronger, but also much more brittle than the α phase, while the γ phase is very brittle, and at the same time weaker than the β body. As indicated by the diagram, alloys containing up to 37 p.c. of zinc, when solidified and in equilibrium, consist of the pure α phase; this is a ductile body whose characteristics closely resemble those of copper itself, but with increasing zinc-content the strength increases while the ductility diminishes slightly. The micro-structure of these alloys closely resembles that of copper; in the cast state they consist of the usual aggregate of roughly polygonal crystals, similar to those illustrated in Fig. 11, Plate I.; as these alloys, however, consist of solid solutions of considerable concentration, they show a strong tendency towards the formation of dendritic 'cores,' as described above. In brass as ordinarily cast this structure is very prominent, and tends to obliterate the ordinary polygonal structure so far as to suggest to the observer, at first sight, that he is dealing with a truly duplex alloy Annealing, however, entirely removes this appearance from the micro-structure, and leaves the alloys perfectly homogeneous; if the annealing has been accompanied by or associated with mechanical work, the disappearance of the 'cores' is accompanied by the formation of numberless 'twinned' crystals which indicate their presence on the micro-sections by the appearance of crystals with rectilinear edges and crossed, by one or more parallel bands showing a distinct orientation, as shown in Fig. 12, Plate I. These structures, it may be added, are also characteristic of the α body met with in other alloys of copper, such as those with tin, aluminium, manganese, &c., although in each class of alloys the range of existence of the α phase may be widely different thus in the copper-aluminium series the range of the pure α phase is only slightly over 7 p.c.

It will be seen that in the equilibrium diagram of the copper-zinc series the region of the pure α phase is bounded on the right by the curved line b_2b_3; immediately to the right of this line lies the region in which the alloys consist of a mixture of the α and β phases. If we consider the cooling from fusion of an alloy containing, for instance, 34 p.c. of zinc, we see that it will begin to solidify at a temperature of about 915°, depositing α crystals until the temperature of the line b_2b_1 is reached at about 880°. At that temperature the remaining liquid solidifies in the form of β crystals, which fill up the interstices between the previously deposited α crystals; if quenched from a temperature just below this line, such an alloy is found to exhibit the duplex structure of α and β thus indicated. On further cooling, however, the alloy crosses the line b_2b_3 and passes from the region of mixed α and β into that of pure α. If time enough is allowed to permit of the establishment of full equilibrium, the whole of the β present in the alloy will be transformed into α and the alloy will become homogeneous in accordance with the indications of the diagram; with most ordinary rates of cooling, however, this transformation is not completed, and the alloy retains some of its original β in that condition, remaining in what is known as 'metastable equilibrium.' In such a case the tendency for the β phase to undergo transformation is always present, but it is held permanently in check by the internal resistance of the metal to such rearrangements—this resistance being very considerable at low temperatures, but diminishing rapidly when the temperature is raised. All metals and alloys in which a transformation or 'inversion' of any kind has been prevented by rapid (or insufficiently slow) cooling, are thus in a meta-stable state, and the attainment of stable equilibrium only requires a raising of the temperature. Alloys which have been quenched are usually intentionally thrown into a meta-stable condition. In the present case it follows that the rate of cooling, in the first instance, or the subsequent application of heat, as in annealing, will make a very great difference to the character of the alloy and to all its physical and mechanical properties, since in the meta-stable state the relatively hard, strong, but brittle β body is present, while in the annealed state this body is absent.

To the right of the line b_2b_3 we have first the region of α and β, and then, to the right of the line b_1b_4, the region of pure β, while beyond that again is the region of $\beta+\gamma$. The industrially important Muntz metal, containing about 60 p.c. copper and 40 p.c. zinc, lies in the region of $\alpha+\beta$, and accordingly always exhibits a very definite duplex structure which is not removed by annealing, in this respect differing from a typical brass such as that used for condenser tubes, which contains 70 p.c. copper and 30 p.c. zinc, and therefore lies in the region of pure α. Study of the curves of the diagram will at once show that the alloys containing the β body during cooling undergo a decomposition on passing through the temperature of the line b_1b_4 or c_1c_2 respectively, breaking up from pure β into α plus β or β plus γ respectively. These decompositions are also readily prevented by somewhat rapid cooling, so that the final state of the alloys depends a good deal upon the rate at which they have been allowed to cool from fusion or from subsequent heating.

Some reference is required to the horizontal line in this diagram, running from P to Q through the entire region of the alloys in which the β phase occurs. This line represents a series of heat-evolutions, which, originally observed by Roberts-Austen (Roberts-Austen, Fourth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1897, 31-100), have been redetermined by Carpenter and Edwards (H. C. H. Carpenter and C. A. Edwards, Journ. Inst. Metals, v. 1911). The nature of the change indicated by these arrest-points is not quite clearly established; the authors just named suggest the interpretation that at this temperature the β phase undergoes decomposition into α and γ, and they quote some microscopical and mechanical evidence in support of this view. There are, however, serious difficulties in the way of this explanation, and the writer prefers to regard the change, for the present, as a transformation in the β phase, and this view has been confirmed by the work of Hudson on vanadium-brass (Hudson, Journ. Inst. Metals, 1914, 1); the critical points in question, however, appear to be of some importance in the thermal treatment of brass.

Before leaving the metallography of the zinc-copper alloys the effect of heat-treatment on the micro-structure of these metals must be mentioned. It has been shown that even at the ordinary temperature the crystals of brass which have previously undergone severe mechanical distortion undergo a gradual rearrangement, resulting in the formation of larger crystals of normal shape (E. Cohen, Revue général des Sciences, Paris, 1910); at higher temperatures this recrystallisation is decidedly rapid, the size of the resulting crystals depending upon both the highest temperature reached and on the duration of heating, although at each temperature there appears to be a limiting size of crystal structure, which is gradually attained, but is not exceeded on prolonged heating at that temperature. For practical purposes the scale of crystal structure is important, because it is a universal law in metals and alloys that increasing size of crystals brings with it decrease in strength and increase in brittleness or fragility. It follows that in brass, as in most other metals, prolonged heating, or heating to an excessive temperature, tends to injure the metal, which becomes 'overheated,' and if the heating is very excessive, may become 'burnt,' a stage where the injury to the internal structure has become so severe that it cannot be eradicated by any treatment short of re-melting.

The influence of the most frequent impurities on brass has received much attention, both from the mechanical point of view and from that of the effect on the micro-structure. A very frequent, and in many respects injurious, impurity is lead. This metal apparently does not remain in solid solution in the α body of the copper-zinc series, and in all ordinary brasses, therefore, appears as a distinct micro-constituent whose presence can be recognised, in the form of minute dark globules, which are readily seen before the specimen is etched, when present to the extent of not less than 0·2 p.c. When the specimens are etched in the more usual manner by means of ferric chloride solution, these minute dark specks are no longer very conspicuous; on the other hand, their presence can be made very obvious by etching the specimens with concentrated nitric acid, applied in the form of a single drop, and immediately washed off in a rapid current of water. This reagent develops a more or less deep and irregular pit in the surface at the spots previously occupied by lead globules, and the etched specimen accordingly appears to be deeply pitted. It may be mentioned that the presence of lead—at all events when present in quantities exceeding 0·40 p.c.—tends to produce 'pitting' by corrosion of the brass around the lead globules, a process which frequently leads to the rapid failure of such objects as condenser tubes, &c. The method of etching a polished specimen with strong nitric acid mentioned above thus furnishes an approximate guide to the probable behaviour of such metal—a brass which pits deeply under such etching is likely to pit rapidly in service. It should, however, be mentioned that these minute lead globules are not the only impurities which cause pitting under the action of strong nitric acid, minute globules of oxide behave in the same manner, although their appearance before etching is different from that of the lead particles. It has, further, been shown that the presence of 2 p.c. of lead may be an advantage in condenser tubes from the point of view of resistance to corrosion (Second Report to the Corrosion Committee of the Institute of Metals, Journ. Inst. Metals, 1913, ii. 13-118). Lead is also intentionally added to brass when specially good machining properties are required.

With regard to other impurities, it may be stated generally that the less injurious or non-injurious ones are rarely if ever visible as distinct constituents under the microscope; in fact, the question whether a given impurity is injurious or not is very largely a question of whether it does or does not form a distinct micro-constituent. Thus arsenic (in small amounts), nickel, silver, &c., all remain in solid solution in the α body—some of these, indeed, as well as manganese and tin and iron are deliberately added to certain 'special' brasses in order to obtain valuable ternary alloys. The constitution of these ternary alloys has not yet been studied sufficiently to make it possible to discuss their metallography in detail, although much work has been done on them (*see* L. Guillet, Alliages Métalliques, ch. x.).

The alloys of copper and tin constitute one of the most complex of the binary series, but their constitution has been exhaustively studied and the results are embodied in the diagram reproduced in Fig. 19. Space does not permit of a full description and discussion of this diagram (Heycock and Neville, Phil. Trans. 1903, 202, A, 1; Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii. 209; Shepherd and Blough, J. Phys. Chem. 1906, 10, 630; J. L. Haughton (Journ. Inst. of Metals, 1915, xiii. 1, 222-248), and attention must again be confined to that end of the series which embraces the industrially useful alloys, which, with the exception of 'speculum metal,' contain less than 14 p.c. of tin.

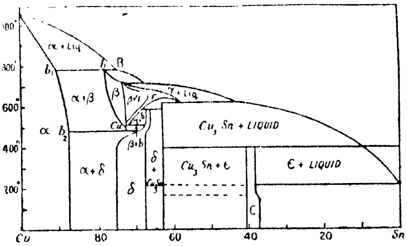


FIG. 19.

The industrially most important alloys are included among those which begin to solidify along the branch AB of the liquidus; these alloys begin to solidify by the deposition of crystals of the α body, which is a simple solid solution of tin in copper. These alloys which contain more copper than the concentration indicated by the abscissa of the point b_1 (about 92 p.c. of copper) completely solidify in the α form and undergo no further changes on cooling to the ordinary temperature. This α body of the tin-copper series is, it may be remarked, somewhat similar in character to the corresponding body of the zinc-copper and aluminium-copper series, *i.e.* a tough ductile body of gradually increasing strength and hardness as the proportion of the added element is increased; there is, however, a marked difference between the three series as regards the relative influence of various proportions of the added element—the concentration of the point corresponding to b_1 in Fig. 19 being in the zinc-copper series approximately 70 p.c. of copper. This may be expressed by saying that the effect of 7 or 8 p.c. of tin is equivalent to that of 30 p.c. of zinc. It is interesting to note that this relatively feeble action of zinc is met with in other alloys of this metal.

Alloys still belonging to the group represented by the line AB but containing more than about 8 p.c. of tin, do not solidify completely until they reach the temperature of the line b_1bB (just below 800°), and at that temperature the remaining liquid solidifies in the form of the β constituent. In the field $bb_1b_2c_4$ the alloys thus consist of a mixture of the two phases α and β, but if they are cooled sufficiently slowly, the β body disappears entirely. In the case of alloys lying between 92 and 87 p.c. of copper, the cooling alloy crosses the line b_1b_2, which is exactly analogous to the corresponding line b_2b_3 of the zinc-copper diagram; on crossing this line the β body disappears and the alloys again consist entirely of α. Since in these as in all similar alloys, the β body is much more brittle than the α, this transformation has a powerful effect on the mechanical properties of the alloys. A still more important change takes place in the alloys containing rather less than 87 p.c. of copper; in these, along the line b_2c_4 the β body is transformed into the δ phase, and this phase is considerably harder and very much more brittle than the β phase. When these alloys are slowly cooled in the ordinary course, these transformations occur only to a limited extent, and the resulting structure shows a mixture of transformed and unchanged constituents, while the mechanical properties are also intermediate. By quenching the alloys containing less than 87 p.c. of copper from a temperature just above the line b_2c_4, however, the β - δ change can be entirely prevented, very much to the advantage of the strength and ductility of the alloys.

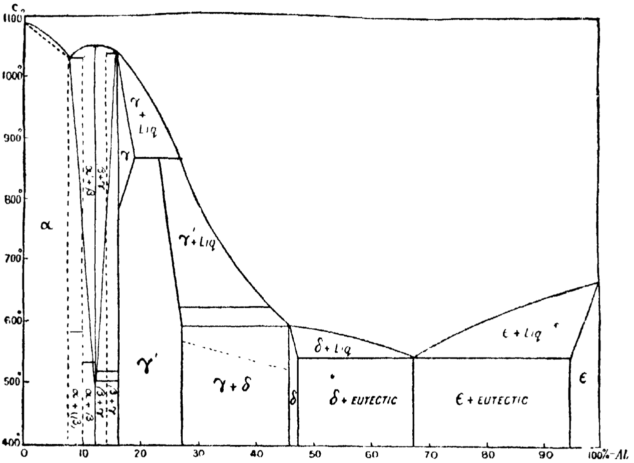


FIG. 20.

Tin-copper alloys to which other metals or metalloids have been added include a number of important 'special bronzes,' many of which are known under trade names. Among the special bronzes, the class of alloys known as 'phosphor bronze' are perhaps the most important. The addition of phosphorus to copper-tin alloys is usually made in the form of either phosphor-copper or phosphor-tin alloys previously prepared. The quantity of phosphorus introduced varies according to the purpose for which the alloy is intended. In a great many cases the object of adding the phosphorus is simply to free the metal from oxide of tin, which is apt to occur in ordinary bronze in the form of small angular crystals the presence of which reduces the strength and ductility of the alloy. Phosphorus thus added merely as a de-oxidising agent passes almost completely into the slag, and mere traces are found in the resulting 'phosphor-bronze.' In other cases it is desired to retain a certain amount of phosphorus, probably in the form of the hard and brittle compound Cu_3P in the resulting alloy, in order to increase its hardness and to give it the special properties desired in a bearing metal—properties which are obtained by alloys consisting of crystals of a hard brittle constituent embedded in a soft and comparatively plastic matrix. The constitution of the copper-tin phosphorus alloys has been studied to some extent, but the reader must refer to the original paper of Hudson and Law (Hudson and Law, A Contribution to the Study of Phosphor-Bronze, Journ. Inst. Metals, iii. 1910, 1, 161) for further details.

The alloys of copper with aluminium (aluminium bronzes) can only be very briefly considered here. The equilibrium diagram, as given by Carpenter and Edwards (Carpenter and Edwards, Eighth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1906), is reproduced in Fig. 20. Again, industrially useful alloys are only found near the extreme ends of the series, but in this case the light alloys of aluminium containing up to 12 p.c. of copper are of importance, as well as the heavy alloys rich in copper (89 p.c. copper and over). The remarkable properties of these alloys and of others directly derived from them have been closely studied (Carpenter and Edwards, Eighth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1906; Rosenhain and Lantsberry, Ninth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1910). From the point of view of constitution and micro-structure, the copper-aluminium series is closely related to the copper-zinc and copper-tin series. Near the copper end of the series we have again an α body consisting of a solid solution of aluminium in copper and gradually increasing in strength and hardness with increasing content of aluminium, but with the important difference that the degree of combined strength and ductility obtainable by the aid of aluminium is much greater than that found in either of the two other series named. An additional property of very great value is the high resistance of these alloys to corrosion. In the copper-aluminium series we again have a β body, which is hard and comparatively brittle, while great brittleness, rendering the alloys industrially useless, appears with the occurrence of the third phase of the series.

The micro-structures of all the copper alloys which have been described above are very similar. Those alloys which consist of the α constituent alone show a structure closely resembling that of pure copper, already illustrated in the case of brass in Figs. 11 and 12, Plate I. Where the β phase is present, etching usually does not reveal the crystal boundaries of the α phase at all, the β constituent being merely darkened and eroded. A typical example from the aluminium-copper series is given in Fig. 21, Plate II. It should be remembered that the scale of this micro-structure will depend, in any given alloy, upon the heat treatment which the metal has received; prolonged heating, especially at high temperatures, produces a coarse structure, and this coarsening of the micro-structure is accompanied by a degradation of the mechanical properties.

The alloys of aluminium have acquired a considerable degree of importance which later developments tend to increase. Only a few of the most important ones can be discussed here. The alloys of aluminium with copper have already been mentioned; their constitution is represented by the right-hand side of the diagram of Fig. 20. It has been found that aluminium possesses a small, but not definitely ascertained power of dissolving copper in the solid state; at concentrations above 5 p.c., however, the copper forms a eutectic alloy with aluminium, the copper being present in this eutectic in the form of the definite compound $CuAl_2$, which—like almost all inter-metallic compounds—is a hard and brittle body. Alloys of aluminium containing as much as 3 and 4 p.c. of copper contain small quantities of this eutectic, and as a consequence they are harder and stronger, but also far less ductile than pure aluminium. When the copper content exceeds 4 p.c. the degree of brittleness becomes too great for many purposes, and the alloys can no longer be rolled into bars or sheets, even when hot.

The alloys of aluminium with manganese have not been studied sufficiently for the construction of a complete equilibrium diagram, but sufficient is known of their constitution to state that in the alloys near the aluminium end of the series, manganese is present in the form of the hard, brittle compound Al_3Mn, and additions of more than 2 p.c. appear to be injurious. Alloys containing from 30 to 60 p.c. of manganese have the curious property of disintegrating spontaneously; a cast ingot of such an alloy, whilst hard and sound when first solidified, breaks down spontaneously into a fine crystalline powder, in some cases in the course of a few hours. This process is not accompanied by any considerable oxidation, and appears to be the result of a polymorphic change of the compound Al_3Mn. Similar spontaneous disintegration occurs in certain other alloys of aluminium, notably those of iron, but in certain cases this change is permanently inhibited if an ingot of the alloy is forged or otherwise worked soon after casting. Certain other, more complex, alloys of aluminium exhibit a process of spontaneous change leading to gradual weakening in the course of several years, so that aluminium alloys should only be employed after a careful study of the properties of the particular combination in question. As regards many of the better-known alloys of aluminium, such as those with copper, copper-manganese, and zinc, this study has already been carried out, so that reliance can be placed on these materials.

The structure and constitution of ternary alloys of aluminium with both copper and manganese has been studied (Rosenhain and Lantsberry, Ninth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1910), but the matter cannot be dealt with here. An interesting development from the alloys of this group is represented by the material known as 'Duralumin,' a patented alloy of aluminium with copper, manganese, and a small amount (about ½ p.c.) of magnesium. Treated in the ordinary manner this alloy is very similar in properties to the simple aluminium-copper alloys, but after heating to a definite temperature lying in the neighbourhood of 400° the alloy undergoes an ageing process occupying 8–10 hours, in the course of which it increases nearly 100 p.c. in strength and hardness without a corresponding loss of ductility. The metallographic explanation of this phenomenon has not, as yet, been arrived at.

The alloys of aluminium with zinc, and derivatives of these alloys, have received much attention (Rosenhain and Archbutt, Aluminium-Zinc Alloys, *v. supra*). The equilibrium diagram of the aluminium-zinc series is given in Fig. 22. Owing to the fact that zinc is soluble in solid aluminium up to a considerable concentration (exceeding 40 p.c.) a considerable range of these alloys is industrially useful, and even the more brittle members of this series may be of practical utility as casting alloys on account of their comparative lightness and cheapness. The liquidus curve of the aluminium-zinc series is given by the line ABCD (Fig. 22). Along AB a solid solution of zinc in aluminium begins to crystallise; up to about 40 p.c. of zinc the solidification is completed in this form (the γ phase) along the curved solidus Ab_1. The break in the liquidus at B, however, indicates that beyond this point the liquid alloys deposit a new phase (β), which is probably the definite compound Al_2Zn_3; along the line Bb_2b_1 this compound is formed by a reaction between the solid γ phase already present and the residual liquid; since the solid crystals become encased in sheaths of the compound, the completion of this reaction is very slow, and in fact only takes place when the alloys are annealed for several hours at a temperature just below that of the line Bb_1. At the point b_2 the alloy possesses the composition of the compound, and the whole of the solid solution reacts with the whole of the residual liquid to form the compound; to the right of b_2 there is an excess of the original solid solution, and this forms an unbroken series of solid solutions with the compound—*i.e.* the compound and aluminium are mutually soluble in all proportions. To the left of the point b_2 there is an excess of liquid, and this solidifies as the eutectic of zinc and the compound along the line d_1c_1. The compound (β) is, however, again decomposed—throughout the entire range of its existence, even in the state of solid solution—on reaching the temperature of the line EFG (256°), when it breaks up into its constituents, viz. the α and γ phases, which are simply saturated solid solutions of aluminium in zinc and *vice versâ*. An interesting feature of this decomposition, however, is that the two products arrange themselves in the form of fine laminæ closely resembling the typical structure of a eutectic alloy, but on a much smaller scale. This phenomenon presents a striking analogy to the formation of 'pearlite' in steel (*v. infra*), and is of importance because of its rarity. How far this decomposition occurs in those alloys of most industrial importance (viz. those containing less than 30 p.c. of zinc) is not yet definitely known, but it is probable that the phenomena in question affect the behaviour of these alloys on heating and cooling.

Iron and **Steel.** The iron-carbon system is, from the metallographic point of view, one of the most complex groups of alloys; although a range of only 5 or 6 p.c. of carbon-content is to be studied, since alloys richer in carbon cannot at present be prepared, and although probably a larger amount of investigation has been expended on these alloys than on any other system, it cannot be said that their metallography is as well understood as that of such alloys as copper-zinc or copper-tin. The reason probably lies in the difficulty of studying the constitution of these alloys at high temperatures—difficulties which are due to the rapidity with which they undergo oxidation at high temperatures, and the rapidity with which many of them undergo transformations on cooling through certain temperatures. Quenching such alloys fails to maintain them entirely in the condition which it is desired to study, and a series of complex transition products are accordingly met with, which vary in character according to the exact circumstances, and have consequently given rise to much controversy. The metallography of the iron-carbon series will be described from the standpoint of the so-called 'allotropic theory,' which is now almost universally accepted, but it is desirable to mention the fact that somewhat divergent views are held in some quarters; these divergences, however, affect only the interpretation and not the actual facts of iron and steel metallography.

The equilibrium diagram of the iron-carbon series, somewhat modified from that originally drawn up by Roozeboom (Roberts-Austen, Fifth Report to the Alloys Research Committee of the Inst. Mech. Eng. 1899; Roozeboom, Zeitsch. physikal. Chem. 1900, 34, 437; Goerens, Erstarrungs und Erkaltungsvorgänge bei Eisenkohlenstofflegierungen Halle, 1907; Carpenter and Keeling, Journ. Iron and Steel Inst. 1904, I) is shown in Fig. 23. It should be remarked at once, however, that this diagram represents what is not in reality a diagram of completely stable conditions; the stable equilibria are indicated by the dotted lines in the diagram, and will be dealt with later, but the meta-stable equilibria represented by the full lines occur with such persistence, especially in the alloys containing less than 2 p.c. of carbon, that they are of greater interest and importance than the conditions of true stability, which are met with in practice only in the case of cast iron and pig irons generally.

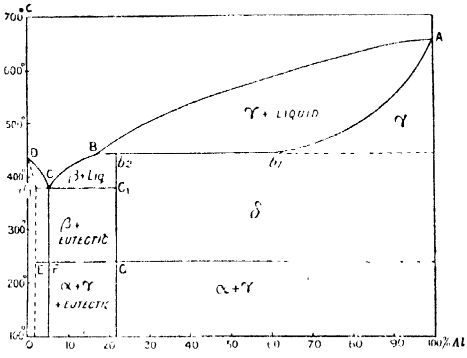


FIG. 22.

The liquidus curve of the iron-carbon alloys, within the limits open to investigation, consists of two branches, AB and BC, the former representing the commencement of solidification of a solid solution of carbon or of iron carbide in iron; the branch BC as drawn in Fig. 23 represents the solidification of carbide of iron (or 'cementite'). This branch of the curve probably tends to a definite maximum at a concentration corresponding to the formula Fe_3C, but this portion of the curve cannot be pursued up to that point, principally because with these high concentrations of carbon the stable system, in which iron carbide or cementite has no place, tends to predominate, and the liquidus curve becomes that representing the separation of graphite according to the dotted line B′C′. Along the line b_1Bc_1 the eutectic of the solid solution (AB) and of cementite (C) separates, while the

PLATE II.

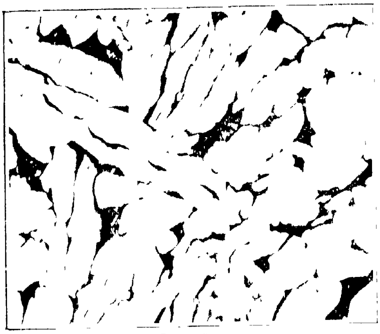


FIG. 24.

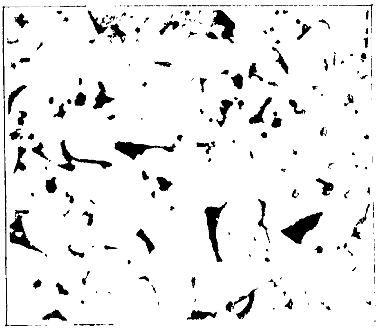


FIG. 25.

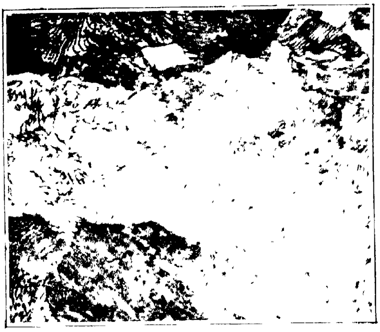


FIG. 26.

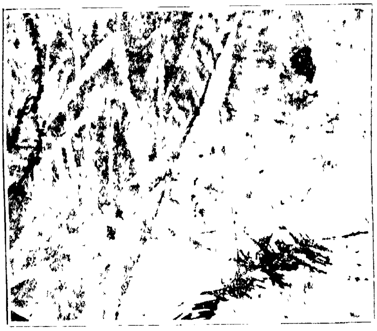


FIG. 27.

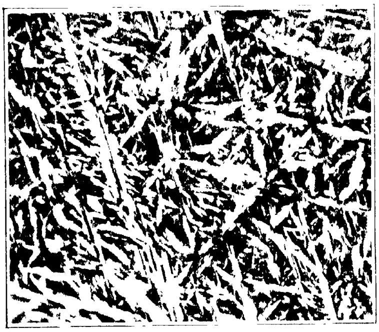


FIG. 28.

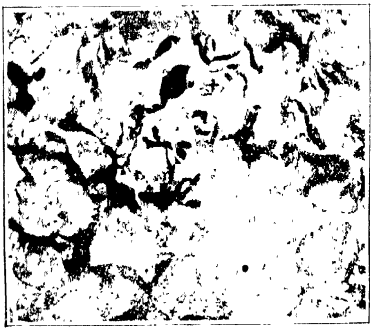


FIG 29.

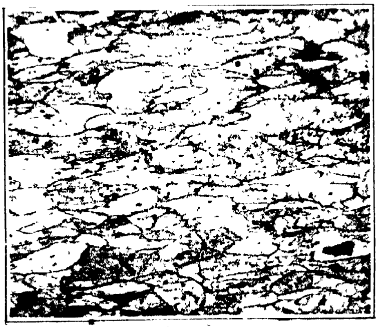


FIG 30.

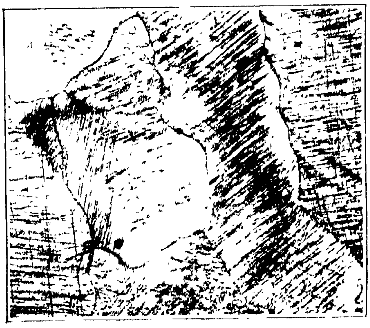


FIG. 31.

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curved solidus line Ab_1 represents the completion of solidification of the alloys containing up to 2·2 p.c. of carbon. The position of this line has been determined by Gutowsky by means of

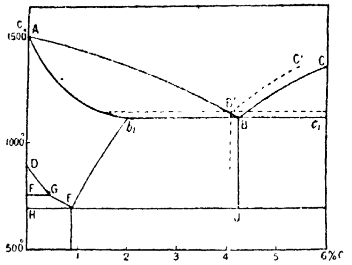


Fig. 23.

quenching experiments (Gutowsky, Metallurgie, 1909, 6, 512), and it is of considerable practical importance since it indicates a superior limit above which steel may not be heated without permanent injury due to 'burning'—steel which has been heated to the point of incipient fusion (*i.e.* above the line Ab_1) appears to be permanently spoilt in such a way as to be unfit for any use except re-melting It may be added that even at considerably lower temperatures steel may be rendered weak and brittle, but if the injury has not gone too far the quality of the metal can be restored by suitable treatment

To understand the lower portion of the diagram of Fig. 23, *i.e.* the portion comprising the lines DE, Eb_1, FG, and HEJ, we must first consider the transformations undergone by pure iron in cooling from a temperature above 900° down to the ordinary temperature. The cooling-curve of electrolytic iron nearly free from impurities is shown in Fig 24. At or near the temperature of 900° there is the first arrest-point in the cooling-curve; then the cooling proceeds regularly down to a temperature of 750° (point F in Fig. 23), where there is a second arrest-point which sometimes exhibits a double peak; if even a trace of carbon is present there is a third very slight arrest-point at or about 700°, and after that the iron cools normally. The interpretation to be placed on these arrest-points is that at the temperatures in question the iron undergoes a transformation or rearrangement of its constituent atoms, which liberates a considerable quantity of latent heat, thus producing the arrest of cooling. These transformations or atomic rearrangements are analogous to similar phenomena observed in such elements as sulphur, selenium, &c., and are described as 'allotropic' transformations. In the case of iron, the form which is stable—in pure iron—at temperatures above 900° is called γ iron, and the arrest-point which indicates the transformation of γ iron is called Ar_3 on cooling and Ac_3 on heating (Osmond, Journ. Iron and Steel Inst. 1890, I). The form of iron which exists between this arrest-point and the next (Ar_2–Ac_2) is called β iron, while the form which exists below Ar_2, down to the ordinary temperature, is called α iron. No marked difference in crystalline form has as yet been demonstrated between the three allotropic modifications of iron, but the point Ac_2 coincides with the disappearance of magnetic permeability on heating and Ar_2 with its re-appearance on cooling, so that β and γ iron are generally regarded as being non-magnetic. It has also been shown that the transition of nearly pure iron from the α into the β form is accompanied by a slight but definite increase in hardness and tensile strength, while a strongly-marked and sudden increase in strength occurs when the iron passes into the γ state (Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910; Rosenhain and Humfrey, Journ. Iron & Steel Inst. 1913, i. 219–271), and it is also known that the allotropic transformations are accompanied by sudden changes in volume. It further follows from the equilibrium diagram of Fig. 23 that while γ iron can hold carbon or carbide of iron in solid solution to a considerable extent, both β and α iron have little or no power of dissolving carbon or carbide of iron.

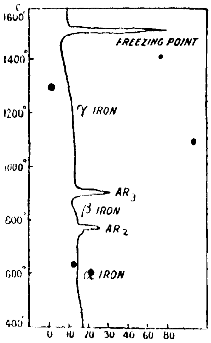


Fig. 24.

The area $ADEb_1$ of the diagram of Fig. 23 thus represents a region in which the alloys consist of a solid solution of carbon or more probably carbide of iron in γ iron. On cooling, this solid solution behaves very much like a liquid solution of two metals; along the line DG crystals of β iron are deposited, leaving the solid solution richer in carbon; along the line GE this process is continued except that the crystals which separate are now α iron; along the line Eb_1, on the other hand, crystals of cementite (carbide of iron) are deposited, leaving the residual solid solution poorer in carbon than it previously had been. If we follow the cooling of a steel containing from 0 to about 0·45 p.c. carbon, we find it passing first through the line DG, and then commencing to deposit crystals of β iron; these crystals increase in quantity until the line FG is crossed, when the whole of the β iron is transformed into α iron, and the quantity of this α iron now continues to increase, the carbon becoming more and more concentrated in the residual solid solution. This concentration continues in such a way that at any instant if a horizontal line be drawn representing the temperature of the alloy, then the abscissa of the point where this line crosses the line DGE indicates the concentration of the residual solid solution. Accordingly, when the steel has reached the temperature of the line HEJ, the residual solid solution has at the same time reached both the concentration and the temperature of the point E. This point, and, indeed, the whole line HEJ, corresponds closely to the eutectic line of a simple system of eutectiferous alloy, such as the line DE of Fig. 4. At the temperature of the line HEJ the remaining γ iron of the residual solid solution undergoes transformation into α iron, and rejects the carbide which it held in solution up to that temperature; the result is that the residual solid solution breaks up into two phases, viz. α iron and cementite, giving rise to a regular laminated eutectic-like structure, which is called a 'eutectoid.' The micro-constituent corresponding to this decomposition is called 'pearlite,' from the pearly appearance which its laminated character gives it under certain conditions of illumination. The α iron, on the other hand, which has previously separated, is known micrographically as 'ferrite,' since it is practically pure iron. The microscopical appearance of pure ferrite has already been illustrated in Figs. 9 and 10, Plate I.; Fig. 25, Plate II. shows the structure of a very mild steel, containing about 0·15 p.c. carbon and consisting of ferrite (light) and pearlite (dark). Fig. 26, Plate II. shows the 'eutectoid' structure of pearlite more highly magnified.

Alloys lying between the concentrations of points E (0·9 p.c. C), and b_1 (2 p.c. C) undergo a somewhat similar series of changes, but here it is cementite which separates out at all temperatures below the line Eb_1, while the residual solid solution is lowered in carbon content until the temperature of the line EJ, and the concentration of the point E are again simultaneously reached. The alloys of this group accordingly consist, when slowly cooled, of crystals of cementite embedded in the eutectoid pearlite.

Alloys lying to the right of the point b_1, so far as they follow the equilibria of the cementite system at all, consist, immediately below the line Bb_1, of crystals of the solid solution of cementite in γ iron embedded in a true eutectic of cementite and solid solution. The subsequent behaviour of these alloys is similar to that of the group just previously described, the solid solution behaves exactly like that of an alloy having the concentration b_1, the additional cementite remaining unchanged throughout. After slow cooling through the line EJ these alloys consist of two kinds of cementite, viz. that derived from the original eutectic solidification and that deposited by the solid solution during cooling, the latter being embedded in pearlite.

The constitution of the iron-carbon alloys at high temperatures, as indicated by the equilibrium diagram, is of special importance, owing to the wide use in the arts and industries of the process of hardening steel by quenching. It has already been explained that the effect of quenching is to inhibit the occurrence of those changes which take place in the metal in the course of normally slow cooling; this inhibition may be more or less complete according to the vigour of the quenching process employed. A very rapid cooling, as by quenching in water or even in iced brine, prevents the transformations more completely than more moderate rates of cooling caused by plunging the hot steel into oil or mercury (Benedicks, Journ. Iron and Steel Inst. 1908, ii. 152).

The iron-carbon alloys in the region ADGEb_1 of the diagram consist, as has already been stated, of a homogeneous solid solution of carbide of iron in γ iron. This solid solution, so far as it is known in micro-sections, has received the name of 'austenite.' In the case of certain alloy steels containing considerable proportions of such elements as nickel or manganese, this austenite solid solution remains stable down to the ordinary temperature, or may be retained by moderate quenching. In pure carbon steels it is never preserved unchanged by quenching, but it has been observed by etching steel surfaces at a temperature of over 1100° by means of hydrogen chloride acting in an atmosphere of hydrogen (Baykoff, Révue de Métallurgie, 1910). In quenched carbon steels, austenite is only met with if the carbon content is over 1 p.c., the quenching temperature over 1000°, and the quenching a vigorous one. Even then the austenite is always accompanied by some of the transition products which are intermediate between the unaltered solid solution (austenite) and the normal final decomposition product, pearlite. Among these transition products, three definite stages are observed. The first of these is the constituent known as 'martensite.' This always accompanies austenite in severely quenched carbon steels, and appears in the form of jagged areas showing a minute structure of fine interlacing needles or laminæ, generally crossing at angles approaching 60°. An example of the austenite-martensite structure of severely quenched carbon steels is shown in Fig. 27, Plate II. In the case of steels of lower carbon content, this constituent, martensite, may appear entirely without austenite, and it may occupy the entire area of the specimen. A photograph of a typical martensite structure is shown in Fig. 28, Plate II. This constituent is the hardest body met with in carbon steels; it is distinctly harder than austenite, but while austenite appears to be non-magnetic, martensite is distinctly magnetic, and it is, in fact, this constituent to which the large coercive force of hardened steel is due. The nature of martensite has been much discussed, but a rational view appears to be that the acicular structure arises from a partial decomposition of the austenite along the cleavage planes of its crystals, the whole process, however, being complicated by the changes in volume which accompany the allotropic transformations of iron.

The γ iron of austenite tends, on cooling, to undergo transformation into α iron. In the course of this transformation the iron probably passes through the β condition, even when the composition of the steel is such that the β iron would have no range of stable existence during slow cooling. As there is some evidence to show that β iron is harder than α iron, the view has been widely held that the hardness of martensite, *i.e.* of hardened steel, is due to the retention in it of a considerable quantity of meta-stable, hard β iron. The difficulty of accounting for the magnetic properties of hardened steel on this theory was met by the hypothesis that the non-magnetic properties of β iron above Ac_2 are the result, not of any inherent non-magnetic quality of β iron, but arise from a large temperature-coefficient of magnetic properties in this form of iron—so that, retained forcibly down to the ordinary temperature, β iron might prove to be sufficiently magnetic to account for the relatively low permeability met with in hardened steel. As simpler explanations have been put forward, however, the 'β iron' theory of hardening in steel has lost ground very considerably in recent years.

The simplest and most logical explanation of the phenomena of hardening in quenched steel is based on what has come to be known as the 'amorphous theory' of metals. This theory is based on the hypothesis, first put forward by Beilby (Beilby, numerous papers; *see* The Hard and Soft State in Solids, Faraday Soc. June, 1904, and same title, Journ. Inst. Metals, 1911, 2 [vi.]) that metals, while ordinarily crystalline, may under certain conditions exist in a non-crystalline or amorphous state in which their properties resemble those of hard, brittle vitreous bodies such as glass or fused silica. (For a full statement of the theory, *see* Rosenhain, Metals, Crystalline and Amorphous, Engineering, Sept. 1913.) Such amorphous metal never exists in considerable masses, but is formed as the result of mechanical disturbance of crystalline arrangement (*see* below) or remains as a very thin residual layer where adjacent growing crystals meet, acting—in the latter case—as an inter-crystalline cement holding the crystals together. The strength and hardness of this cementing layer accounts for the fact that in pure metals the crystal junctions are stronger than the crystals themselves, so that the metal becomes stronger and harder the greater the number of junctions, *i.e.* the smaller the scale of the crystal structure. In the extreme case, where the crystals themselves are little more than incipient nuclei, we should have the maximum amount of junction area and—according to the amorphous theory—the largest amount of hard, amorphous metal, so that the metal would attain its maximum hardness in that condition. Now this is precisely the condition which may be expected to arise during the quenching of steel. The transformation from γ iron to a iron takes place, during slow cooling, by the development of a number of small a crystals which grow larger and absorb more and more of the γ iron. When cooling becomes very rapid, however, there is no time for the growth of these a crystals, and in these circumstances a very much larger number of a nuclei would come into existence, but each would remain little more than a nucleus, surrounded by its layer of amorphous cement. The fullest hardness would thus be attained if the rate of cooling and other conditions were such that the whole volume of the steel was finally occupied by these minute or incipient a crystals merely separated from one another by films of amorphous metal. In any actual case, however, the size of the developed a crystals, and the number of nuclei formed, would vary even in different parts of a single original γ crystal, thus giving rise to the acicular structure of martensite, which is undoubtedly related to the crystalline planes of the austenite from which it is derived. On this theory, the hardness of quenched steel is ascribed to the presence in it of a relatively large amount of amorphous metal, thus correlating the hardness obtained by quenching with the hardness produced by plastic deformation ('cold work') and with the hardness of such substances as glass. It is interesting to note that both quench-hardened and work-hardened metals are softened by tempering and annealing, and that when hardness of either kind is extreme it is liable to undergo slight changes even at the ordinary temperature ('ageing'). Finally, it may be pointed out that the magnetic properties of hardened steel are readily accounted for by the 'amorphous' theory; the nuclear crystals of a iron are the seat of permeability and 'remanence,' while the high coercive force or magnetic hardness is due to the fact that the magnetic atoms (or molecules) of a iron lie tightly embedded in the hard and unyielding amorphous cement which hinders re-arrangement of any kind, whether under the action of mechanical forces (hardness) or under the action of magnetic forces ('coercivity').

Even if we may regard the amorphous theory as adequately explaining the phenomenon of hardening in quenched steel, other factors undoubtedly play an important part. Thus, the volume-changes which are known to accompany the transformations of iron from the γ to the a state produce powerful internal stresses in quenched steel, which frequently lead to distressing failures in the shape of 'hardening cracks' or, in less severe cases, to distortion. These internal stresses may play a part in the hardening process, although this part is probably confined to facilitating the production or retention of amorphous metal. Thus Carpenter and Edwards (Carpenter and Edwards, The Hardening of Metals, Journ. Iron and Steel Inst. 1914, i. 138-191) ascribe the hardness of quenched steel to the presence of amorphous iron, but consider that this is formed as the result of mechanical deformation by multiple twinning (*see* below) of which they believe that the micro-structure of martensite bears evidence. McCance (A. McCance, The Theory of Hardening, Journ. Iron and Steel Inst. 1914, i. 192-205) goes still further and ascribes the hardness of steel, without reference to amorphous metal, to a state of 'inter-strain' set up within the material by quenching.

It is further evident that carbon must play a vitally important part in the whole phenomena of hardening since they do not occur to any very considerable extent in the absence of that element.

Carbon is said to act as a species of 'brake' on the allotropic transformations, and the nature of its action may be understood when it is considered that the transformation of pure iron from one allotropic form to another merely involves a rearrangement of the atoms within the crystal. While the γ iron contains dissolved carbide of iron, however, the allotropic change of the iron involves the expulsion of the carbide from solution, and, for completion, its rejection from the crystals of iron. This rejection involves a transfer of the carbide molecules across distances which are very large compared with molecular dimensions, and it is not difficult to understand that such a transfer occupies time, and that it is, therefore, more or less readily inhibited by the action of quenching.

In the case of martensite the rejection of the carbide from its state of solution in the γ iron of the austenite has only just begun, and the carbide probably exists in a separated form only on the cleavage planes of the original γ iron crystals. When the rate of cooling has been somewhat slower, however, the rejection of the carbide, as well as the allotropic transformation of the iron itself, are allowed to go somewhat further, and as a result a further transition product is found in the micro-sections. This is the dark-etching body known as 'troostite,' found in oil-hardened steels, and particularly in those quenched at the temperature of the thermal transformation. In this constituent the rejection of the carbide is practically complete, but the carbide is in a state of extremely fine division, according to some views, indeed, in a state of 'colloidal solution' or suspension in the iron (Benedicks, Journ. Iron and Steel Inst 1905, ii. 352, and 1908, ii. 217). In troostite it appears probable that while some γ iron is still present and a considerable amount of hard amorphous iron is present as cement surrounding the minute α crystals, yet these crystals have had time to grow to a certain extent, with the result that steel containing troostite is distinctly softer than that consisting entirely of martensite. When the quenching or tempering is so adjusted that the whole of the γ iron has just disappeared, the proportion of troostite would attain its maximum, this being the state of tempered steel called 'osmondite,' by Heyn (Heyn and Bauer, Journ. Iron and Steel Inst. 1909, i. 109). Further tempering, or still slower cooling, leads to the appearance of a further transition product, which is not very sharply differentiated from troostite on the one hand, and from pearlite on the other. This is known as 'sorbite.' Here almost the whole of the iron has reached the α stage, and the carbide has begun to segregate into masses which are at first too minute to be seen under the microscope; but with further tempering, or less vigorous cooling, the segregation of the carbide reaches the point where it can be resolved under the microscope into granular or laminated pearlite. Steel containing sorbite is not really hard in the ordinary sense, although it possesses distinctly greater hardness and tensile strength than the same steel in the pearlitic state. Rail and other comparatively low-carbon steel is sometimes so treated as to render the carbonaceous constituent sorbitic, and in this condition the steel exhibits specially valuable physical properties.

The hardening of steel may be summarised metallographically as follows:—

Fully hardened steel—Martensite or austenite martensite.
Moderately hardened or slightly tempered—Martensite-troostite.
Tempered steel—Troostite with either martensite or sorbite.
Slightly hardened or much tempered—Sorbite.

A large and increasingly important class of alloys are those produced by the addition of various metals, such as nickel, chromium, manganese, and the rare metals such as vanadium, tungsten, molybdenum, and others, to iron and to certain grades of steel. The metallography of these steels is, however, so complex that it cannot be described here. Broadly speaking, these 'special' steels may be divided into four large classes, the class to which any particular steel belongs being dependent upon the total proportion of alloyed elements present. The first class of the special steels are those containing relatively small proportions of the added elements; these possess a simple structure of ferrite and pearlite, very similar to that of pure carbon steels, although differing in minor details; their mechanical properties are frequently markedly superior, and notably those containing nickel, chromium, and vanadium are finding much technical application. The great value of the nickel and nickel-chrome steels of this type lies in the fact that by heat-treatment, such as quenching in oil from such a temperature as 820°C. followed by tempering at or near 600°C. they attain excellent physical properties which cannot be obtained in carbon steels. This is partly due to the action of nickel and chromium in not only lowering the critical points of the steel, but in retarding the rate at which the steel undergoes its transformations. This makes it possible to 'quench' satisfactorily with less risk of fracture and to obtain good results from heat-treatment even in large masses of steel which can never be made to cool very rapidly. The second class of the alloy steels show a structure resembling that of martensite; they are hard and practically unworkable, but their existence is utilised in certain special cases, as in the production of case-hardened objects without quenching in the cementation of certain grades of nickel steel. The third class of alloy steels are those containing still larger proportions of alloyed elements, as, for example, a nickel steel containing about 25 p.c. of nickel. They exhibit a simple polyhedral structure, which is that of austenite, but in this case the solid solution contains the alloyed elements as well as the γ iron and carbon. These steels are non-magnetic, and possess remarkable mechanical properties, notably a high degree of ductility combined with great tensile strength. In some cases, however, they possess the peculiar property of being converted into steels of the previous class (martensitic) by mechanical work; such a steel, when first cut by a saw, for instance, is quite soft, but it rapidly hardens under the tool, until it can no longer be cut at all. This property is, however, confined to steels lying near the border-line of the two classes. A further increase in the proportion of the alloyed elements brings the steel into the fourth class, in which the presence of a carbide of the alloyed element can be detected in the micro-structure. For most general purposes such steels are useless, but certain of them are extremely valuable for use as high-speed cutting tools. This highly important type of alloy steels cannot, however, be discussed in detail here. It can only be mentioned that while in ordinary carbon steels the temperature required for tempering, and therefore softening the steel is as low as 400°, these special steels can be made to withstand temperatures as high as a dull red heat without losing their hardness; they are thereby enabled to maintain their cutting edge at speeds which render the tools almost red hot. The manner in which the presence of the alloyed elements effects this behaviour can be approximately understood when it is mentioned that the critical points of an ordinary carbon steel are to some extent displaced, according to the temperature to which the steel has last been heated. The presence of an alloyed element not only itself displaces the normal position of the critical points—in the case of nickel steels, for example, extending the range of stable existence of γ iron down to the ordinary temperature—but the alloyed element also increases the extent to which the critical points can be displaced by heat treatment. In the case of high-speed tool steels it is found that by heating the steel to a temperature of 1200° or higher (a white heat), and allowing it to cool in a current of air, the critical point on next heating is raised to so high a temperature that a dull red-heat does not affect the 'temper' of the steel.

The micro-structure of steel has so far been described as the result of either 'normally slow cooling' or of quenching. For the steels containing higher proportions of carbon this classification is practically sufficient, but for the class of 'mild' steels containing up to 0·70 p.c. of carbon the effects of quenching need scarcely be considered, except in the case of the 'sorbitic' steel mentioned above. On the other hand, for these steels the temperature and duration of annealing, and the application of work by rolling, pressing, or forging is of vital importance, both to the micro-structure and to the mechanical behaviour of the material. Metallographic methods have cleared up the greater part of this field, but only general results can be mentioned. Thus it may be taken as a fundamental fact that coarse and well-defined micro-structures imply undesirable mechanical properties, especially as regards behaviour to shock, while a fine, close structure offers the best prospect of good quality in the metal. It is, however, a universal tendency of crystals forming an aggregate such as iron or steel, to grow; *i.e.* certain of the constituent crystals of the aggregate tend to increase in size at the expense of their neighbours. In the case of such comparatively 'refractory' metals as iron or steel, this growth of crystals is *nil*, or exceedingly slow at ordinary temperatures, although in the case of lead (Ewing and Rosenhain, The Crystalline Structure of Metals, second paper, Phil. Trans. A, 1900) and brass (*see* L. Guillet, Alliages Métalliques, ch. x.), such growth takes place measurably even without the application of heat. When iron or steel is heated, however, the tendency for crystal growth rapidly asserts itself, and, indeed, it is to this process of growth, or of 're-crystallisation,' that we owe the power of annealing or softening metal which has been rendered hard and brittle by the application of cold work. In the case of steel, when the temperature of the upper critical point is passed (on heating) the transformation occurs at a number of centres which behave as centres of crystallisation, and a new system of crystals begins to grow from each of these centres, although to some extent the new set of crystals tends to follow the outlines of those previously in existence. With rising temperature the rate of crystal growth increases, and the ultimate size of structure attained is thus a function of both the time of heating and of the temperature attained. When steel which has been thus heated is allowed to cool slowly, although there is a distinct tendency for rearrangement to occur on passing through the critical points, yet the coarse structure is very apt to persist, and if the heating has been carried too far we have a coarse, weak structure typical of 'overheated' steel. To some extent this coarse structure may be removed by heating the steel for some time to a temperature just above the upper critical point, and then cooling it somewhat rapidly through the critical point down to the ordinary temperature. A more effective method, however, consists in exposing the steel to hot working (rolling, forging, &c.). This process deforms the existing crystals in a manner described below, and these deformed crystals are unstable, *i.e.* crystal growth starts afresh in them, and can no longer follow the previous outlines; the result is an entirely new and much more minute system of crystals. The exact analogue of this process has been watched, in the case of lead, taking place at the ordinary temperature.

For the mere removal of the hardening effects of 'cold work' annealing temperatures between 600°C and 700°C. are frequently used, particularly as these are found to leave the steel softer than higher annealing temperatures. The use of these temperatures, however, entails serious disadvantages. The very soft state of the steel when thus annealed is due to a very low elastic limit which—in very low carbon steels—approximates to that of annealed pure iron. The reason is that annealing in the temperature range just below the critical point, Ac, has the effect of allowing the lamellæ of cementite which exist in the pearlite to separate and to form small granules or globules, which—on prolonged annealing—coalesce into larger globules. In this form, divorced from its former close union with the ferrite, the cementite can no longer exert its stiffening and strengthening effect on the surrounding ferrite, and the steel is reduced to the state of iron in which globules of cementite are uselessly embedded. Such over-softened steel can, however, readily be brought into a very satisfactory condition by 'normalising' it, *i.e.* heating to 900°C. followed by cooling in air.

Another class of phenomenon sometimes occurs in very mild steel when annealed at these low temperatures after mechanical deformation ('cold work'). This is known as 'grain growth' (*see* Sauveur, Note on the Crystalline Growth of Ferrite below its Thermal Critical Range. Proc. of the International Ass. for Testing Materials, Sixth Congress, 1912, ii.; Chappell, Journ. Iron and Steel Inst 1914, i. 460; Rosenhain and Hanson, (Journ Iron and Steel Inst. 1918, i. 313). It consists in a very rapid development of large, coarse ferrite crystals. This development occurs most freely in ferrite free from all carbon, as it exists in pure iron or in steel containing little or no carbon. Even in steels containing as much as 0·3 p.c. of carbon, however, bands or 'ghosts' are often found in which no carbon is present, and in these grain-growth of a dangerous kind may occur. Here also the evil can be completely cured by normalising at 900°C.

Cast Iron, Pig Iron. The equilibrium diagram and constitution of iron-carbon alloys has so far been discussed only in reference to alloys containing less than 2 p.c. of carbon, and usually known under the name of 'steel.' The alloys richer in carbon must now be dealt with; these are met with industrially in the shape of a large variety of cast and pig irons, but it must be remembered that while the better kinds of steel consist essentially of almost pure iron-carbon alloys, the cast and pig irons generally contain very considerable proportions of impurities, such as silicon, sulphur, phosphorus, &c. In addition, a large number of these higher-carbon alloys differ essentially from steel by containing carbon in the form of graphite. The equilibrium diagram of the iron-carbon system given in Fig. 23 represents, as has already been mentioned, what is in reality a meta-stable condition of the iron-carbon system; if sufficient time at a suitable temperature be allowed it is probable that carbide of iron would decompose completely into iron and graphite. Apparently it is also possible for free carbon (graphite) to separate as primary crystals from the molten iron-carbon alloys containing over 4·3 p.c. of carbon. If it is true as seems probable that in the liquid alloys the carbon is dissolved in the form of only slightly dissociated carbide, then in these high-carbon alloys the carbide (cementite) in certain conditions, and notably in the presence of silicon and in the absence of manganese, is liable to undergo decomposition at a temperature near that of incipient solidification, one of the products of decomposition being graphite, which thus appears as a solid phase in the shape of crystals separating from the liquid. The equilibrium diagram of this ultimately stable system (Fig. 23, dotted lines) thus contains the liquidus branch corresponding to the separation of the γ iron solid solution, but this is carried to a eutectic point differing slightly from the γ iron-cementite eutectic, and corresponding to a γ iron-graphite eutectic; below the temperature of this eutectic the alloys are completely solid, and to the left of the eutectic-point (B) consist of γ iron embedded in the graphite eutectic, while to the right of the point B they should consist of primary graphite crystals embedded in the eutectic; owing to the low density of the graphite, however, this substance does not remain embedded in the liquid metal from which it is separated, but floats to the surface in the form of 'kish.' On further cooling the behaviour of these alloys should theoretically lead to the complete decomposition of all the cementite, including that contained in the γ iron solid solution, but the exact circumstances in which such decomposition occurs are not fully ascertained. The lower part of the dotted-line diagram of Fig. 23 has not, therefore, been filled in.

In practice certain varieties of cast and pig iron tend to follow the system of solidification just indicated, but they rarely, if ever, do so completely; whilst, if the rate of cooling is rapid, and especially if the iron contains little silicon and much manganese, the decomposition of the cementite is more or less completely prevented, and the iron cools with the formation of little or no graphite, forming what is known as 'white iron'; iron which contains much graphite and little cementite is known as 'grey,' whilst intermediate varieties are known as 'mottled.'

Microscopically, all varieties of iron may, in accordance with the above, be regarded as mixtures of steel with a certain amount of graphite. The 'steel' portion will have the characteristic structure of an iron-carbon alloy whose carbon content corresponds to the amount of 'combined' carbon, *i.e.* of undecomposed cementite, present in the iron. Thus an iron containing, for instance, 0·5 p.c. of combined carbon, together with 3 p.c. of graphite (total carbon 3·5 p.c.), will show a structure of ferrite and pearlite corresponding to that of a 0·5 p.c. carbon steel, together with a considerable amount of graphite. A typical example of the micro-structure of a 'grey' iron of this type is shown in Fig. 29, Plate II., but the presence of impurities, particularly of phosphorus, very materially affects the appearance of such micro-structures, since the phosphorus forms, with the iron, a definite compound Fe_3P, and this compound forms with the iron a well-defined and characteristic eutectic, which may be mistaken for pearlite under the microscope. This phosphide eutectic can, however, be readily distinguished from pearlite by exposing the specimen to a moderate degree of heat which causes a slight surface oxidation, and in consequence a differential tinting of the various constituents.

Increasing total carbon-content, with constant amount of combined carbon, merely causes an increase in the amount of graphite found in the micro-sections; an increase in the proportion of combined carbon, however, causes the 'steel' portion of the iron to move up the carbon-scale, first producing an increase of the amount of pearlite, and finally the appearance of cementite in place of ferrite. In the case of 'white' irons produced by chilling high-carbon cast iron, the graphite disappears entirely, and the resulting micro-structure consists entirely of cementite and pearlite, together with the constituents due to impurities. As regards mechanical properties, it is obvious that the presence of plates of graphite, destroying the continuity of the 'steel' matrix, largely reduces the strength of the material as compared with a steel of equal combined carbon; on the other hand, the iron will be 'soft' or 'hard,' according to the micro-structure of the 'steel' matrix, an iron containing ferrite and pearlite will be much softer and less brittle than an iron containing cementite and pearlite. These latter constituents are responsible for the great hardness of 'chill' iron castings.

For certain purposes castings are treated in such a manner as to be deprived of their graphite content more or less completely by a process known as the production of 'malleable' castings. This process consists in heating or annealing the castings for a considerable time, generally while packed in an oxidising material, such as iron oxide. To a considerable extent decarburisation occurs, while much of the combined carbon is deposited in the form of a very finely divided graphite known as 'temper carbon.' The softening effect of the process depends partly upon the actual removal of carbon by oxidation and partly upon the effect produced by prolonged heating upon the arrangement of the graphite which remains in the metal. While in ordinary castings it is present in the form of plates and veins, in 'malleable' castings it is found in small nodules and patches which do not affect the strength and ductility of the material to anything like so great an extent.

A converse process, for producing surface hardness in articles made of iron or mild steel is that known as 'case hardening.' In this process the iron or steel is heated for a considerable time in contact with carbonaceous matter, preferably also containing nitrogenous matter. The iron takes up carbon and forms a hard external layer rich in carbon, which, therefore, has the power of being hardened by quenching. Micro-sections of case-hardened articles readily show the depth and nature of the hard 'case,' and the structure of the underlying softer and tougher material.

Deformation, fracture, and fatigue in metals. Microscopic metallography has made it possible to determine the mechanism by which metals undergo plastic deformation, and incidentally to explain the mode of fracture under tension, shock, and 'fatigue.' It has already been indicated that when a piece of metal is forced to change its shape, as by hammering, rolling, pressing, &c., the component crystals of the metal also undergo a corresponding change of shape, although subsequently if the temperature is high enough to permit of sufficient molecular mobility in the particular metal in question, the crystals tend to rearrange themselves into more normally shaped forms. If a bar of metal be forcibly stretched, the constituent crystals will be found to be stretched also. Thus cold-rolled iron shows the structure illustrated in Fig. 30, Plate II, where the ferrite crystals are seen to be lenticular in section in place of the normal polyhedral shape. The manner in which metallic crystals undergo such changes of shape becomes evident if a surface of a specimen of metal is prepared for microscopic examination (*i.e.* polished) before the piece of metal is subjected to the change of shape. The crystals which, before deformation, appeared as practically featureless polygonal areas, after the application of the strain, are seen to be cross-hatched by systems of fine lines. In the case of highly plastic metals, such as lead or copper, the lines are seen to be characteristically straight and regular, while in the harder metals, such as iron, the lines appear more or less branched and curved. It has been possible, however, to observe the formation of these lines in iron at high temperatures (up to 1100°) (Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910), and in those circumstances they are as straight and regular as those of copper. The typical appearance of these lines is shown in Fig. 31, Plate II. Their nature has been elucidated by a long series of experiments, including the preparation of transverse sections of specimens of metal upon which the lines had previously been developed. The conclusion arrived at is that they are in reality minute steps in the surface arising from the fact that the adjacent portions of the crystal have slipped over one another along the cleavage or gliding planes of the crystal. It may be accepted as abundantly proved that the polygonal grains seen in the micro-sections of metals are true crystals, possessing all the essential features of crystals as regards the regular and symmetrical arrangement of the constituent molecules, although these crystals have grown together into an aggregate without allowing the individual members to develop their characteristic external shape. These crystals, however, may be regarded as built up of minute elements or groups, much as a stack of bricks is built up of individual bricks. It has been shown (Ewing and Rosenhain, The Crystalline Structure of Metals, Bakerian Lecture, Phil. Trans. A, 1899; Rosenhain, Deformation and Fracture in Iron and Steel, Journ. Iron and Steel Inst. 1906, I.; Rosenhain and Humfrey, The Crystalline Structure of Iron at High Temperatures, Proc. Roy. Soc. 1910) that these crystal 'bricks' or units are themselves never deformed or changed in shape (excepting the temporary 'elastic' deformations which are left out of consideration here), and that the crystals which are built up of these units accommodate themselves to changes of shape imposed upon them by allowing the 'bricks' to slide over one another along at least three sets of gliding planes. Where these planes of slip reach the surface of a crystal forming part of the previously polished face of the specimen, the result is the formation of a minute step in the surface, and the short sloping surface of such a step, when viewed by 'normal' light, appears as a fine dark line. Illumination by oblique light, on the other hand, shows the lines shining brightly against the dark background whenever the short sloping surfaces are turned so as to face the incident light. On account of their mode of formation these lines have been called 'slip bands.'

In certain metals, notably in copper and its α alloys, and also in lead and many other plastic metals and alloys, the process of deformation by slip as just described is also accompanied by what is known as 'mechanical twinning.' In this process a certain portion of the crystal, in order to accommodate itself to the circumstances created by the application of plastic strain, swings over into an entirely new orientation, which is, however, definitely related by crystallographic laws to the orientation of the parent crystal; this process usually occurs in a series of parallel bands. The presence of crystals showing regular alternating bands of similar orientation is always an evidence of 'twinning,' and since twinned crystals rarely occur in cast metals, this feature is generally evidence of the application of work to the specimen in which it appears. Where deformation by slip and by mechanical twinning occur together, the slip-bands change their direction on passing the edge of the twinned area, and a stair-like shape of the bands results.

The process of deformation by slip obviously implies that the metal retains its truly crystalline character after it has undergone a permanent change of shape, and it is found that, unless the amount of deformation has been very large, this is actually the case.

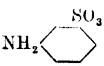
A further series of phenomena must, however, be considered; these relate to the changes which occur in the structure of the crystal at and in the immediate neighbourhood of the surfaces upon which slip has taken place. It has been shown that when the surface of a piece of metal is rubbed or polished (G. T. Beilby, The Hard and Soft State in Metals, Phil. Mag. 1904; G. T. Beilby, Hurter Memorial Lecture, J. Soc. Chem. Ind. 15, 1903), some of the molecules or atoms in the surface layer of the metal are torn away from their crystalline arrangement, and are left upon the surface in a state of relative freedom, which allows them to behave in a manner resembling a thin film of viscous liquid. It is by the spreading out of such a film under the action of pressure and of polishing media, that polished surfaces are formed. The material of this thin surface film, however, is no longer in the crystalline condition; its condition resembles that of an exceedingly viscous liquid, and is therefore to be regarded as being truly 'amorphous,' and it has been shown that in this amorphous condition, although temporarily mobile, the material is much harder and also much more brittle than the same substance in the crystalline state. Now in the interior of the crystals of a metal which undergoes deformation by slip, metal surfaces move over one another under very considerable pressures, and it follows that an action very similar to that which occurs upon a surface which is being polished will take place on every gliding plane; *i.e.* a thin layer of atoms will be disturbed from their normal position in the crystalline arrangement, and a layer of temporarily mobile, amorphous material will be formed. Now it has been shown that if this layer is thin, the directive forces of the adjacent crystalline systems are sufficient to cause the disturbed atoms to reassume the orientation of the system, and in that case the surface on which slip has taken place may be said to have 'healed up.' On the other hand, two different cases may occur. In the first case the process of slip may be carried so far that the disturbed layer becomes too thick to allow of complete and almost immediate recrystallisation, and then each surface of slip remains as a species of 'scar' within the metal, taking the form of a thin layer of hard, amorphous material. The presence of these hard layers tends to render the metal both harder and stronger, but also more brittle, and it is well known that this is the universal result of the application of cold work or plastic deformation to ductile metals. If the process of plastic deformation is carried to an extreme, as in the hammering of thin metal foil, a large proportion of the metal may ultimately be present in the amorphous condition; but this condition is unstable, and a very moderate amount of heating is sufficient to induce recrystallisation. This stage, however, is only reached in special circumstances; more usually the application of stress results first in a certain amount of plastic deformation (by slip), followed by a local and rapid deformation—also by slip—which culminates in fracture at some point where the amount of slip has carried the adjacent parts of a crystal out of contact. The fracture resulting from such a mode of breaking has a fine silky fibrous appearance, owing to the fact that all the minute surfaces of slip along which fracture has occurred are inclined at small angles to the direction of stress, but the metal has remained essentially crystalline; indeed, apart from non-metallic inclusions, such as the 'cinder' in wrought iron, there is no true 'fibrous' structure or condition in metals.

The second class of circumstances which do not permit of the immediate re-crystallisation of the layer of disturbed atoms, which are formed on surfaces of slip arise when the stress which has produced a small amount of slip is reversed; such a reversal of the stress will, if it comes soon after the first occurrence of the slip, cause the reversal of the slip itself, and the layer of disturbed atoms will still be in the mobile condition, and will serve as a species of lubricant to facilitate the return slip. At the same time, the reverse motion will produce an increase in the number of disturbed atoms, and the disturbed layer will grow in thickness with each reversal. After a large number of such reversals of stress some of this disturbed material will be forced—in its temporarily mobile state—out of the space between the adjacent sections of the crystal, and what was before a surface slip will thus become an actual fissure, which spreads rapidly through the whole mass. The resulting fracture will show comparatively large bright facets representing the planes on which slip has occurred, so that the fracture will have a 'crystalline' appearance, although the metal itself is neither more nor less crystalline than it was at the beginning. The view that metals 'become crystalline' under alternating stresses or under vibration is thus entirely without foundation. It should be said that the explanation of the manner in which metals fracture under 'fatigue,' *i.e.* under the repeated alternation of stresses which would fail to fracture the material at a single prolonged application, as it has been given here is no longer to be regarded as of a speculative character, since every point in the explanation has been definitely observed and verified by several independent observers (Ewing and Humfrey, The Fracture of Metals under Repeated Alternations of Stress, Phil Trans A, 1903, 200; Stanton and Bairstow, The Resistance of Iron and Steel to Reversals of Direct Stress, Proc. Inst C.E. 1907).

The conception of the part which amorphous metal plays in the whole mechanism of the cohesion of crystalline aggregates in general, and of metals in particular, has in recent years received considerable extension by the development of what has come to be known as the 'Amorphous Cement' theory (Rosenhain and Ewen, Intercrystalline Cohesion in Metals, Journ. Inst. Metals, 1912, [viii.] 2, 149–185; same authors and title, Second Paper, Journ. Inst. Metals, 1913, [x.] 2, 119–149; Rosenhain and Humfrey, The Tenacity, Deformation, and Fracture of Mild Steel at High Temperatures, Journ. Iron and Steel Inst. 1913, [i.] 219–271; Bengough, A Study of the Properties of Alloys at High Temperatures, Journ. Inst. Metals, 1912, [vii.] 2). According to this view, when a metal solidifies from fusion, or undergoes recrystallisation in the solid state, the crystals grow outward from their respective centres or nuclei, ultimately limiting each other by approaching to contact; actual contact between adjacent crystals, however, only occurs at a few points, a small residuum of the metal being retained in the amorphous or under-cooled liquid condition filling the minute interstices between adjacent crystals and acting as an amorphous cement, whose relatively great strength and hardness accounts for the special strength which is known to reside in the intercrystalline boundaries in pure metals. That such a residue of uncrystallised materials should remain in the crystal junctions is ascribed to the counterbalancing effect of opposed crystalline orienting forces emanating from the two adjacent crystals, but considerable difference of opinion exists, even among the supporters of the theory, as to the probable thick[illegible] of these hypothetical layers of amorphous cement. Although at first put forward essentially as a working hypothesis to account for certain special facts, so large a volume of evidence has since been brought forward in support of the theory that considerable importance must now be attached to it, particularly as it is found that this conception brings together under a single, simple explanation a very wide range of otherwise apparently unconnected facts, such as the modes of fracture of metals both at the ordinary temperatures and at temperatures near their melting-points, their behaviour *in vacuô*, and the action of certain gases on metals.

The methods of metallography, although they have so far been described largely from the point of view of affording a clearer insight into the nature and constitution of metals and alloys, are also capable of direct practical applications. These applications include, in the first place, the control of metallurgical operations, particularly of the temperatures employed in thermal and mechanical treatment of all kinds and the investigation of new alloys. There is also an important field of usefulness for these methods, and more especially for the microscopic examination of metals in conjunction with exhaustive mechanical tests, in the investigation of cases of failure or breakage either under test or in service, including such questions as apparently mysterious fractures, unduly rapid wear or corrosion and similar problems. Although it would be too much to claim that metallographic methods are always capable of finding the correct solution of problems of this class, a great deal of light can often be thrown upon the causes which have led to the failure, and, in many instances, the true cause of failure can be discovered. A considerable number of such investigations have been described (W. Rosenhain, The Study of Breakages, Engineering, Sept. 1908; W. Rosenhain and D. Hanson, A Cause of Brittleness in Mild Steel Boiler Plates, Journ. Iron and Steel Inst. 1918, I.), but the greater number are—for obvious reasons—never allowed to reach the public. It is, however, to be borne in mind that it is largely by the investigation of cases of unexpected breakage or other failure that fresh knowledge on the properties of our engineering materials can be obtained. In a number of actual cases it has been found that the metal had been damaged by modes of treatment which had been regarded as harmless. Metallography is therefore a science which has not only placed in the hands of metallurgists a mass of valuable and detailed knowledge of the internal structure and constitution of metals and alloys, but it has also furnished them with methods of investigation which are probably destined to elucidate many of the still 'mysterious' features in the behaviour of the materials of engineering. W. R.

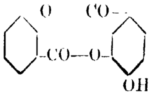
METANIL YELLOW *v.* Azo- colouring matters.

METANILIC ACID  Prepared by sulphonating nitrobenzene and reducing the nitrobenzene sulphonic acid by iron turnings, neutralising with milk of lime, filtering, and evaporating. Used for making metanil yellow.

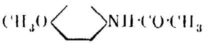
METARABIN *v.* Gums.

METAXYLORCINOL *v.* Phenol and its homologues.

METELLAGIC ACID. Metellagic acid $C_{14}H_6O_5$ is prepared by the oxidation of *m*-hydroxybenzoic acid with potassium persulphate and sulphuric acid. It crystallises from pyridine in colourless prismatic needles, and when distilled with zinc dust gives fluorene. The acetyl derivative $C_{14}H_5O_5(C_2H_3O)$, colourless needles, melts at 269°–271°. According to Perkin and Nierenstein (Chem. Soc. Trans. 87, 1425), metellagic is related to ellagic acid, and possesses the following constitution:



METHACETIN. *p* Methoxy acetanilide



An antipyretic and analgesic.

METHAL *v. Spermaceti*, art. Waxes.

METHANE. *Methyl hydride* (*v.* Methyl compounds).

METHOXYBENZENE. *See* Anisole.

***p*-METHOXYBENZENEDIAZO CYANIDES** *v.* Diazo- compounds.

METHOZIN. A synoym for antipyrine.

METHYL, CH_3, is a univalent, compound radicle, not known in the free state. The compound C_2H_6 discovered by Frankland and Kolbe (Chem. Soc. Trans. 1, 60) was called methyl, and believed to be the free base, and even when its molecule was recognised as dimethyl $(CH_3)_2$, it was at first thought to be distinct from ethane, the gas obtained by Frankland from ethyl iodide by heating with zinc and water. It was, however, proved to be identical with that body by Schorlemmer (Chem. Soc. Trans. 17, 262).

Methyl Compounds.

Methyl acetate *v. Alkyl acetates*, art. Acetic acid.

Methyl alcohol CH_3OH. *Methyl hydrate, hydroxymethane, wood spirit, pyroxylic spirit, wood naphtha*, 'Columbian spirit,' 'Colonial spirit,' 'Manhattan spirits,' 'kakol' (proprietary names in U.S.A.); 'green wood spirits' and 'standard wood spirits' in Canada, 'prospirit' in Germany (Ger. *Holzgeist*). B.p. 64·56°/760 mm. (J. Gyr, Ber. 1908, 4322); 64·96° (corr.) (Thorpe and Rodger); sp.gr. 0·796472 at 15°/15° (Klason and Norlin, Chem. Soc. Abstr. 1906, i. 821; Gyr, Ber. 1908, 4322; Doroschewsky and Roschdestvensky, Chem. Soc. Abstr. 1909, i. 868); 0·81000 at 0°/4° (Young and Fortey, Chem. Soc. Trans. 1902, 735); m.p. −94·9° (Ladenburg and Krugel); H.C.=170·6 (Stohmann, Kleber, and Langbein, J. pr. Chem. [ii.] 40, 341); H.F.=61·4 (S., K., and L.).

Boyle found that the liquid obtained by distilling wood contained two constituents, an acid portion and a neutral spirit. Various conjectures were made as to the nature of this 'spirit,' the first investigation of which was made by Dumas and Peligot in 1834 (Ann. Chim. 58, 5; 61, 193). They gave it the name 'methyl alcohol' (μέθυ, wine; ὕλη, wood).

Formation.—By the dry distillation of wood, of beet-sugar molasses (Vincent, Bull. Soc. chim. [ii.] 27, 148), or of calcium formate (Paternò and Lieben, Annalen, 167, 293; Friedel and Silva, J. 1873, 526). Methyl alcohol occurs in the free state and as methyl esters in plants (Gutzeit, Maquenne, Geuther), forming various essential oils. It is also recovered from the waste water of the steamed wood pulp in paper manufacture, by allowing the liquors to concentrate through repeated use and subsequently distilling (Alkier, Eng. Pat. 1514, 1890). According to Takahashi, Gunke, and Yamazaki (J. Amer. Chem. Soc. 1917, 39, 27231), most fermented drinks contain small quantities of methyl alcohol.

Preparation.—Methyl alcohol is prepared on the large scale from the distillate from wood, which contains various tarry matters, acetic acid, and the methyl alcohol. The distillates from the wood are allowed to stand for some time, when the tarry, resinous, and oily matters precipitate; the supernatant liquid is then filtered through gravel into another vessel, from which it is either distilled at once or after previous neutralisation with lime. The distillation is effected in the first case in copper stills, and heat is applied by coils of copper pipes conveying steam, in the second case boilers of sheet iron are employed, and the heat applied by the direct fire.

The distillate is then purified by repeated redistillations from caustic lime, and lastly, from a little sulphuric acid (in order to remove NH_3 and amines). In some cases chalk is used instead of lime, and sometimes chalk and sodium bicarbonate.

The distillation is carried on in copper stills heated by steam coils, or the retorts are guarded by iron jackets, and heated over the fire. The crude spirit thus obtained is colourless, and its sp.gr. varies from 0·87 to 0·82.

The disagreeable-smelling constituents are sometimes got rid of by Wildsmith's process, which consists in the application of oxidising agents, *e.g.* potassium dichromate, aided by the action of light, to the crude spirit, by which means the hydrocarbons, &c., are destroyed, and a colourless, almost odourless, liquid obtained.

The usual yield of pyroxylic spirit is from 1 to 3 gallons from each ton of wood distilled, but the quantity depends upon the kind of wood employed, and also upon the proper regulation of the temperature during distillation. The best yields are obtained by using a mixture of oak, beech, and hornbeam (Barillot, Compt. rend. 122, 469).

In the United States birch, beech, maple, oak, elm, and alder are used, together with sawdust and wood-waste. The wood is seasoned for 1 to 2 years and cut into lengths of 50 inches, which are distilled in iron retorts at 200°–260° (*see* WOOD, DESTRUCTIVE DISTILLATION).

Large quantities of methyl alcohol are now made by the distillation of vinasse (residues obtained by the evaporation of the spent wash in the preparation of ordinary alcohol from beet-sugar molasses). The distillate contains ammoniacal compounds, methylamine, methyl cyanide, and methyl alcohol. After neutralising with sulphuric acid the mixture is evaporated, the vapours being condensed; these contain methyl cyanide and methyl alcohol; the former is decomposed by rectification over lime, and the distillate, which contains dilute methyl alcohol, is dehydrated by means of lime. Methyl alcohol is also formed in the manufacture of wood pulp and from waste esparto liquors.

Commercial wood spirit contains very variable proportions of the pure alcohol, from as low as 35 p.c. to as high as 95 p.c. It contains acetone, methyl acetate, and formate, allyl alcohol, aldehyde, methylamine, and often various empyreumatic bodies; these have considerable influence, not only upon its density, but also upon its solvent powers for shellac and other resins. The 'tailings' contain furfural, methyl-ethyl ketone, and allyl acetate with small quantities of paraxanthine. The crude alcohol has a sp.gr. of 0·796–0·875 at 15·5°. The purest spirit is always preferred for use in lamps as a fuel, but for the use of the varnish-makers and polishers some of the impurer varieties, containing essential oils, &c., are sometimes chosen.

The following process for the production of methyl alcohol from wood is patented by F. J. Root (U.S. Pat. 713552, 1902). In the destructive distillation, a pressure is maintained in the apparatus slightly lower than that of the atmosphere. The readily condensable gases are condensed in primary condensers, whilst the gases which are not readily condensable are mixed with a definite proportion of steam and the acids thus set free are recovered in a secondary condenser. The degree of vacuum and the supply of steam required for mixing with the less condensable gases are obtained by means of a steam exhauster situated beyond the primary condensers. This exhauster is regulated automatically by the volume and tension of the gases generated so that both functions are kept constant. The introduction of superheated air, containing only a little oxygen and a good deal of steam, which increases the yield of volatile products in the ordinary destructive distillation, is patented by Zwillinger (Eng. Pat. 18823, 1889).

A variant of the ordinary method of destructive distillation of wood consists in first adding strong sulphuric acid. 100 kilos. of wood, containing 35 p.c. of moisture, with 20 kilos. of strong sulphuric acid on distillation up to 160° and rectifying the distillate, yield wood alcohol 3 kilos., acetic acid 7 kilos., oil of turpentine 2 kilos., and 40 kilos. of wood charcoal of good quality (Orljavacer, Chem. Fabrik, Fr. Pat. 357432, 1905).

Hofer and Moest find that a good yield of methyl alcohol is obtained by the electrolysis of sodium acetate solution containing sodium chlorate (Annalen, 323, 284; D. R. P. 138442, 1901).

The conversion of methane, which often occurs in large quantities near oilfields, into methyl alcohol or other commercially useful articles, is a problem which is still undergoing investigation. Lance and Elworthy (Eng. Pat. 7297, 1906) claim the use of hydrogen peroxide (with or without ferrous sulphate or monopersulphuric acid) and monopersulphuric acid alone. Von Unruh has utilised atmospheric air as an oxidising agent with bark as a catalyst, but in this case methyl alcohol is the subsidiary product, the oxidation proceeding further and producing formaldehyde chiefly. 24 litres of methane by this process, when mixed with 180 litres of air at 45°, yield in the apparatus described 1565 grams of formaldehyde in 12 hours (U.S. Pat. 891753, 1907; *see also* Hausmann & Co., D. R. P. 214155, 1906).

Attempts have been made to chlorinate natural methane under the action of light and to hydrolyse the methyl chloride produced to methyl alcohol, but without economic success (*cf.* Walter, D. R. P. 222919; Bedford, J. Ind. Eng. Chem. 1916, 10, 1090). Methyl chloride can be completely converted to methyl acetate by passing it over porous sodium acetate at about 295° and into methyl alcohol by passing it over slaked lime at 300°.

Purification.—According to a method patented by Piper and Rotten of Berlin (D. R. P. 36827, 1886), the wood spirit is first distilled with lime and then by fractional distillation, the acetone is thus reduced to 1 or 2 p.c. To remove the remaining acetone the spirit is heated to boiling (with reflux condenser), and dry chlorine is passed into it; portions are tested from time to time by distilling, and testing the distillate for acetone by the iodoform reaction (*see also* Rotten, J. Soc. Chem. Ind. 1901, 604). Treatment with bleaching powder is also sometimes adopted. When this reaction is no longer given the passage of the chlorine is stopped, and the methyl alcohol separated by fractional distillation from the high boiling chlorinated acetone, and purified by distillation over lime from traces of chlorine. The methyl alcohol thus obtained is perfectly free from acetone; the chloracetone can be reconverted into acetone by reducing agents. Methyl alcohol purified in this way invariably contains some chlorinated impurities, which may be removed by heating under a reflux condenser with lime.

In order to obtain pure methyl alcohol, the oxalic or formic ester is prepared, and then decomposed by heating with water (Wöhler, Annalen, 81, 376), or ammonia (Grodzki and Kramer, Ber. 7, 1494). Methyl benzoate when heated with a solution of 1 part sodium hydroxide in 5 parts of water yields methyl alcohol (Carius, Annalen, 110, 210). Pure methyl alcohol may be prepared by treating 10 parts of commercial wood spirit with 1 part of iodine, and then adding caustic soda until the colour of the iodine disappears, and distilling (Regnault and Villejean, Bull. Soc. chim. [ii.] 42, 255). 100 c.c. of the crude spirit are digested with 150 grams of solid caustic soda, and afterwards distilled, 500 grams of oxalic acid are mixed with 200 c.c. of sulphuric acid, and then 400 c.c. of the purified alcohol are added, and the mixture is heated on the water-bath; the crystals of methyl oxalate are dried by pressure and saponified by heating with water at 70°. The distillate is then dehydrated by means of baryta, lime, and anhydrous copper sulphate (Dittmar and Fawsitt, Trans. Roy. Soc. Edin. 33, 509). Apparatus for the purification of wood spirit is best constructed of aluminium or an aluminium alloy free from copper. Copper heavily coated with tin, or iron or copper lined with earthenware may also be used with connecting pipes of earthenware. Air should be excluded as completely as possible, as this oxidises the methyl alcohol to formaldehyde, acetaldehyde, and methylal, the reaction being readily catalysed by copper vessels. Aldehyde resin is likely to form in the still if the alkaline reagent has been added to the crude wood spirit (P. Pikos, J. Soc. Chem. Ind. 1909, 1118).

The following is a continuous method of preparing pure concentrated wood spirit. The crude spirit is distilled and the vapours passed first through lime water, then warm concentrated alkali solution (15°–20° Beaumé), afterwards washed with stearic or other fatty acid, and finally with alkali again. This treatment removes all aldehydic resins, higher alcohols, ketones, &c. (J. Farkas, D. R. P. 166360, 1904).

The purest anhydrous methyl alcohol is prepared from the best acetone-free commercial article by first heating for some time with freshly burnt lime, then leaving in contact with ignited potassium carbonate for some weeks, and finally, distilling several times from metallic calcium. The most accurate criterion of dryness is the esterification constant which, for the anhydrous alcohol and phenyl acetic acid, is 3·556. One-twentieth of a p.c. of water by volume lowers this to about 0·532 and ordinary pure dry methyl alcohol from methyl oxalate is often as low as 0·465 (J. Gyr, Ber. 1908, 4322).

Other processes are patented by Rosencrans (U.S. Pat. 793512, 1905); Chute (U.S. Pat. 824906, 1906), Schmidt (U.S. Pat. 885183, 1908); and Christiansen (U.S. Pat. 1302011, 1919).

Detection and estimation.—The recognition of methyl alcohol itself is a somewhat difficult matter but its oxidation products, formaldehyde and formic acid, are more readily characterised. Of its compounds, the most characteristic is the *oxalate*, which is a crystalline solid melting at 54°. Mulliken and Scudder (Amer. Chem. J. 1899, 21, 266; 1900, 24, 444; J. Amer. Chem. Soc. 1905, 892), Barbet and Jandrier (Chem. Soc. Abstr. 1898, ii. 265), Jandrier (Chem. Zentr. 1899, i. 1296), Leach and Lythgoe (J. Amer. Chem. Soc. 1905, 964), Scudder and Riggs (*ibid.* 1906, 1202), Franz Utz (Chem. Zentr. 1905, ii. 1467), Hinkel (Analyst, 1908, 417), Voisenet (Bull. Soc. chim. 1906, [iii.] 35, 748), Trillat (Compt. rend. 1899, 127, 232), Voisek (J. Soc. Chem. Ind. 1909, 823), Pieszczek (Pharm. Zeit. 1913, 58, 850), Denigès (Compt. rend. 1910, 150, 530, 831), Bono (Chem. Zeit. 1912, 36, 1171), Mannich and Geilmann (Arch. Pharm. 1916, 254, 50), Wolff (Chem. Zeit. 1919, 43, 555), Ehman (Amer. J. Pharm. 1919, 91, 594), Simmonds (Analyst, 1912, 37, 16), Jones (*ibid.* 1915, 40, 221), Gettler (J. Biol. Chem. 1920, 42, 311), and others have all made contributions to the question of the most reliable test for methyl in the presence of ethyl alcohol (*cf.* Simmonds, Alcohol, Macmillan & Co., 1919). As an outcome, the following official test of the U.S. Pharmacopœia has been adopted for quantities of 2 p.c. and upwards: the liquid is diluted so as to contain about 10 p.c. total alcohols. About 3 c.c. is oxidised by plunging a red hot copper spiral five or six times into it while it is kept from boiling away by being surrounded by a beaker of cold water. It is then filtered and boiled till free from the smell of acetaldehyde. After cooling, 1 drop of 0·5 p.c. resorcinol is added and sulphuric acid poured into the test tube so as to form a layer. It is allowed to stand for 3 minutes and gently rotated. If no rose-red ring appears, methyl alcohol is below 2 p.c. Quantities from 2 p.c. down to 0·1 p.c. may be detected by fractionating 50 c.c. three times through a good fractionating head. The first two distillations should proceed till about 35 and 20 c.c. respectively in the case of a strong spirit, or 20 and 10 c.c. with a weak one, have passed over. The first 3 c.c. of the third distillation is tested as above.

The detection of methyl alcohol in the presence of formaldehyde necessitates first the removal of the formaldehyde. This may be done in several ways. Gnehm and Kaufler (Chem. Soc. Abstr. 1904, ii. 520; 1905, ii. 209) recommend combining it with sodium sulphanilate. Stritar (*ibid.* 1904, ii. 686) uses ammonia. Bamberger (*ibid.* 786) prefers sodium hydrogen sulphite. The best reagent for this purpose is probably potassium cyanide, as proposed by Leffmann (Chem. Zentr. 1905, ii. 1467). The methyl alcohol is subsequently distilled off and estimated by the sp.gr. of the distillate. *See also* Duyk (Chem. Soc. Abstr. 1902, ii. 110) and Blank and Finkenbeiner (Ber. 1906, 1326).

A review of the various methods of detecting methyl alcohol in presence of ethyl alcohol is given by Simmonds, 'Alcohol,' Macmillan & Co., which also contains a description of the process of Denigès, as modified by Simmonds, and adopted in the Government Laboratory, London. The book contains a useful bibliography on the subject. Chaplin has also described a modification of Denigès' method, which is claimed to increase its sensitiveness and to avoid false reactions (Analyst, 1921, 375). The solution to be tested is diluted until it contains 5 p.c. of total alcohols; 5 c.c. of this solution are then mixed with 0·3 c.c. of 85 p.c. phosphoric acid, and 2 c.c. of 3 p.c. potassium permanganate solution are added. When the permanganate is decomposed completely (about 10 minutes) 1 c.c. of 10 p.c. oxalic solution is added, followed, after 2 minutes, by 1 c.c. of concentrated sulphuric acid and 5 c.c. of Schiff's reagent. If a blue or violet coloration does not appear after 10 minutes (any coloration due to acetaldehyde will have disappeared in this time) there is present less than 0·2 p.c. of methyl alcohol in the mixed alcohols.

Table showing percentage of methyl alcohol in aqueous solutions at 15° (Klason and Norlin, Arkiv för Kemi Mineralogi och Geologi. vol. 2, No. 27).

Sp.gr. 15°/15°	P.c. methyl alcohol by wt	P.c. methyl alcohol by vol.
0·7964	100·00	100·00
0·7975	99·64	99·77
0·8000	98·75	99·18
0·8025	97·85	99·59
0·8050	96·96	98·01
0·8075	96·07	97·41
0·8100	95·18	96·80
0·8125	94·28	96·18
0·8150	93·39	95·55
0·8175	92·50	94·92
0·8200	91·60	94·28
0·8225	90·70	93·63
0·8250	89·80	92·98
0·8275	88·88	92·31
0·8300	87·97	91·64
0·8325	87·06	90·97
0·8350	86·16	90·29
0·8375	85·23	89·60
0·8400	84·29	88·88
0·8425	83·34	88·13
0·8450	82·39	87·40
0·8475	81·44	86·64
0·8500	80·47	85·88
0·8525	79·50	85·09
0·8550	78·51	84·27
0·8575	77·50	83·44
0·8600	76·50	82·61
0·8625	75·50	81·76
0·8650	74·49	80·89
0·8675	73·49	80·02
0·8700	72·48	79·13
0·8725	71·44	78·23
0·8750	70·38	77·31
0·8775	69·31	76·39
0·8800	68·25	75·43
0·8825	67·18	74·43
0·8850	66·09	73·41
0·8875	64·98	72·39
0·8900	63·86	71·34
0·8925	62·76	70·28
0·8950	61·65	69·23
0·8975	60·52	68·17
0·9000	59·36	67·09
0·9025	58·20	65·97
0·9050	57·01	64·82
0·9075	55·82	63·65
0·9100	54·64	62·46
0·9125	53·49	61·27
0·9150	52·31	60·04
0·9175	51·10	58·80
0·9200	49·84	57·54
0·9225	48·54	56·20
0·9250	47·20	54·79
0·9275	45·84	53·36
0·9300	44·49	51·92
0·9325	43·15	50·48
0·9350	41·79	49·01
0·9375	40·40	47·53
0·9400	39·00	45·94
0·9425	37·54	44·29
0·9450	36·03	42·66
0·9475	34·51	41·03
0·9500	32·95	39·35
0·9525	31·38	37·61
0·9550	29·79	35·81
0·9575	28·14	33·89
0·9600	26·44	31·82
0·9625	24·66	29·83
0·9650	22·89	27·83
0·9675	21·14	25·76
0·9700	19·38	23·67
0·9725	17·63	21·54
0·9750	15·85	19·40
0·9775	14·03	17·25
0·9800	12·27	15·12
0·9825	10·60	13·04
0·9850	8·94	11·03
0·9875	7·32	9·06
0·9900	5·72	7·13
0·9925	4·18	5·30
0·9950	3·01	3·84
0·9975	1·39	1·69
1·000	0·00	0·00

A table published by Doroschewsky and Roschdeslvensky (J. Russ. Phys. Chem. Soc. 1900, 41, 977) differs in no essential particular from the above table.

For the estimation of methyl alcohol, in the absence of other materials than water, a reference to the table of sp.gr. is the most rapid method, but Zeisel's well-known methyl iodide method is very reliable. The latter is only interfered with by acetal or ethyl alcohol. In the presence of ethyl alcohol the most accurate method is that due to Thorpe and Holmes (Chem. Soc. Trans. 1904, 1), depending on the fact that when oxidised with dichromate and sulphuric acid, ethyl alcohol gives rise to acetic acid and a minute quantity (about 0·5 p.c.) of carbon dioxide, whilst methyl alcohol is completely oxidised, under the stipulated conditions, to carbon dioxide and water. The process is as follows: the sample is mixed with water in such proportion that 50 c.c. of the mixture shall contain not more than 1 gram of methyl alcohol, and in the presence of ethyl alcohol not more than 4 grams of the mixed alcohols. Fifty c.c. of this mixture are then introduced into the oxidation flask, 20 grams of potassium dichromate, and 80 c.c. of dilute sulphuric acid (1 : 4) added, and the mixture allowed to remain for 18 hours. A further quantity of 10 grams of potassium dichromate and 50 c.c. of sulphuric acid mixed with an equal volume of water are now added and the contents of the flask heated to boiling for about 10 minutes. The carbon dioxide is swept out by a current of air and collected in weighed soda-lime tubes. When ethyl alcohol is present, a subtractive correction of 0·1 gram of carbon dioxide for each gram of ethyl alcohol must be made This method is of great convenience in determining the adulteration of tinctures and other medicinal preparations by methylated spirits.

Other substances yielding carbon dioxide in these circumstances are allyl alcohol, methyl acetate, and acetone. Ether and pyridine do not affect the estimation.

Properties.—A colourless liquid with an odour like that of ethyl alcohol; miscible with water in all proportions, and with contraction and evolution of heat (*v.* table). It burns with a blue flame. It possesses, like ethyl alcohol, remarkable solvent powers, dissolving most substances which are soluble in ethyl alcohol; consequently it may be used in many cases instead of that liquid.

Methyl alcohol, like strong ethyl alcohol, is a toxic substance, its poisonous nature being attributed to its conversion into formaldehyde (Bösseken and Waterman). For a bibliography of the literature relating to the toxicity of methyl alcohol, *see* Morson (J. Soc. Chem. Ind. 1918, 26, T). According to Langgaard (Chem. Zentr. 1912, ii. 1382) methyl alcohol is more poisonous than ethyl alcohol when taken in repeated small quantities, but ethyl alcohol is much more dangerous when taken in a single large dose.

Its vapour pressure at various temperatures is given in the following table (Dittmar and Fawsitt):—

Temperature	Vapour pressure	Temperature	Vapour pressure
°C.	mm	°C.	mm.
0°	29·7	40°	259·4
5°	40·2	45°	327·3
10°	53·8	50°	409·4
15°	71·4	55°	507·7
20°	94·0	60°	624·3
25°	122·7	65°	761·1
30°	158·9	64·96°	760·0
35°	203·9		

A similar table, ranging from 0° to 240°, has been published by Young (Scient. Proc. Roy. Dublin Soc. 1910, 440).

Anhydrous copper sulphate is slightly soluble in absolute methyl alcohol, yielding a bluish-green solution, hence it cannot be used as a test of the freedom of methyl alcohol from water (Kelpl, J. pr. Chem. [ii.] 25, 526). This blue solution deposits crystals of $CuSO_4,2CH_3OH$ (Forcrand, Compt. rend. 102, 551). Hydrated copper sulphate dissolves to the extent of 11·5 p.c. at 0° and the solution on standing deposits green rosettes of crystals having the composition $3CuSO_4\cdot CuO,4CH_3OH$ (Auger, *ibid.* 142, 1272). Methyl alcohol combines with many salts in a manner similar to water of crystallisation, *e.g.* $LiCl,3CH_3OH$; $MgCl_2,6CH_3OH$; $CaCl_2,4CH_3OH$, six-sided tables, decomposed by water, may be heated to 100° without decomposition (Kane, Phil. Mag. [iii.] 10, 45). A compound with barium oxide, $BaO,2CH_3OH,2H_2O$, is obtained in brilliant prisms, when BaO is dissolved in aqueous methyl alcohol, and the liquid evaporated at the ordinary temperature (Forcrand, Compt. rend. 102, 1557).

When passed over heated zinc, methyl alcohol yields carbon monoxide, hydrogen, and a small quantity of methane (Jahn, Ber. 13, 983). In contact with heated copper it is decomposed into formaldehyde and hydrogen. A large proportion of the formaldehyde is polymerised to methyl formate, whilst another portion is resolved into carbon monoxide (Mannich and Geilmann, Ber. 1916, 49, 585). At higher temperatures (1150°) it is completely resolved into carbon monoxide and hydrogen, the decomposition taking place in two stages which proceed simultaneously. In the first stage formaldehyde and hydrogen are formed, and the formaldehyde is then decomposed, giving carbon monoxide and hydrogen (Peytral, Compt. rend. 1917, 165, 703). By the action of zinc chloride, hydrocarbons C_nH_{2n+2} are the chief products, also some hexamethyl benzene (Le Bel and Greene, J. 1878, 388). By electrolysis in presence of sulphuric acid, *methylal* $CH_2(OCH_3)_2$ is produced (Renard, Ann. Chim. Phys [v.] 17, 290).

Methyl alcohol is not decomposed by *bacterium aceti.* Potassium or sodium liberates hydrogen and forms a methoxide; sodium methoxide $NaCH_3O$ combines at 160° with carbon monoxide to form sodium acetate.

Magnesium dissolves in methyl alcohol on gently heating, forming magnesium methoxide, which separates in pointed prisms from solutions containing about 6 grams in 40 of alcohol, or as an amorphous powder from more concentrated solutions. The crystals contain 3 molecules of methyl alcohol and effloresce rapidly. Bromine converts it into bromoform and magnesium bromide. Magnesium nitride reacts energetically with methyl alcohol forming trimethylamine, according to the equation:

$$Mg_3N_2+6CH_3OH$$
$$=3Mg(OH)OCH_3+NH_3+N(CH_3)_3$$

(Szarvasy, Ber. 1897, 305, 806).

Chlorine acts on methyl alcohol readily if moist. In diffused daylight at 99·5° the chief product is formaldehyde, which probably results through the intermediate formation of chloromethyl alcohol CH_2ClOH, and dichloromethyl ether $(CH_2Cl)_2O$. The latter may actually be isolated. Carbon dioxide and carbon monoxide and also methyl chloride are continuously evolved during the reaction. If the alcohol is diluted with water the reaction proceeds with explosive violence. Bromine has but little action, but in sunlight at 130°–150° methyl bromide is formed, mixed with carbon monoxide and dioxide and formic acid if the bromine is not in excess.

Iodine is even more inert, but at 180°–200° hydrogen iodide, carbon dioxide, and methyl iodide are formed. The chief bulk of the alcohol is converted into methyl ether, which is also readily produced by heating the alcohol in sealed tubes with 5 p.c. of iodine (André Brochet, Compt. rend. 121, 130).

Cold methyl alcohol absorbs one molecular proportion of boron trifluoride forming *boron methoxy difluoride* $BF_2\cdot OCH_3$, crystallising in prisms melting at 41·5° and boiling at 87°, Sodium methoxide (1 mol.) readily converts this compound into *boron dimethoxy fluoride*

$$BF(OCH_3)_2$$

which is a colourless mobile liquid fuming in air, burning with a green flame, and boiling at 53°. It has a sp.gr. of 1·053 at 0°. Sodium methoxide changes this into *methyl borate* $B(OCH_3)_3$. Methyl borate boils at 55°–56° and has sp.gr. 0·919 at 0°. It burns with a green flame and is readily decomposed by moist air or water.

There is also formed by the action of boron trifluoride on methyl alcohol a molecular compound with methyl ether, $BF_3,O(CH_3)_2$. It boils at 126° 127° and dissociates at a slightly higher temperature. In addition an acid product of still higher boiling point is produced to a small extent (V. Gasselin, Ann. Chim. [vii.] 3, 5).

The catalytic oxidation of methyl alcohol to formaldehyde is the subject of several papers by E. Orloff (J. Soc. Chem. Ind. 1908, 139, 419, 1176). Ozone oxidises methyl alcohol to formaldehyde very readily in 50 p.c. aqueous solution (Harries, Ber. 1903, 1933).

White phosphorus, when heated with methyl alcohol (1 mol.) for some hours at at least 250°, produces tetramethyl phosphonium hydroxide and, in addition, phosphines and phosphoric acid (J. Berthaud, Compt. rend. 143, 1166).

Methyl alcohol decomposes diazonium salts, forming, with benzene diazonium nitrate, anisole, *o*-nitrophenol, and 2 : 4-dinitrophenol. If water is present, *p*-nitrophenol is also formed. The alkoxy derivative only is produced from diazobenzenesulphate. Sodium methoxide in solution in methyl alcohol produces benzene and diphenyl (Beeson, Amer. Chem. J. 16, 235).

Impurities.—The impurities of commercial wood spirit are small quantities of aldehyde, dimethylacetal, allyl alcohol, acetone, methylethyl ketone, higher ketones, and chloroform.

Acetone is the most objectionable, especially when the alcohol is to be used in the preparation of aniline colours. In order to estimate the amount of acetone 1 c.c. of the wood spirit is mixed with 10 c.c. of a double normal solution of soda, and 10 c.c. of a double normal solution of iodine are added with constant shaking, and then 10 c.c. of absolute ether. The ethereal layer is then measured, an aliquot portion taken and evaporated on a watch-glass and the residual iodoform weighed. The weight of the iodoform (calculated to the total volume of ethereal solution) multiplied by 0·28 gives the amount of acetone in 1 c.c. of wood spirit (Kramer, Ber. 1880, 1002).

According to Messenger (Ber. 21, 3366), this method gives too high results if the quantity of acetone be small. The following method and details are due to Milan and Stritar (Zeitsch. anal. Chem. 1904, 387). *Crude wood spirit:* 5 c.c. are diluted to 500 c.c. and 5 c.c. of this mixture are submitted to Zeisel's process. The weight of silver iodide multiplied by 272·9 gives grams of methyl alcohol per 100 c.c. *Aqueous wood spirit* containing under 10 p.c. methyl alcohol: 10 c.c. are diluted to 50 c.c. and shaken for ¼ hour with 0·5 gram of charcoal, filtered, washed, and diluted to 100 c.c. and estimated as above. *Crude pyroligneous acid:* 50 c.c. are neutralised with sodium carbonate made up to 250 c.c. and filtered. 100 c.c. are then made strongly alkaline and distilled till 50 c.c. have collected. The distillate is treated with charcoal, &c., as above. The shaking with charcoal removes guaiacol and other phenol ethers, but the estimation is invalidated by the presence of acetal, methyl acetate, and allyl alcohol. A correction for these may be made by determining the iodine number and esterification number of the sample.

Methyl benzoate $C_6H_5·COO·CH_3$. Prepared by heating a mixture of benzoic acid, methyl alcohol, and sulphuric acid. A colourless liquid, of aromatic smell; b.p. 198·6°; sp.gr. 1·0942 at 15°/15°. Known as 'Niobe oil,' and used in perfumery.

Methyl boride $B(CH_3)_3$, *bormethyl, trimethylborine*, V.D. 1·9108 (calc.=1·9314), a gas obtained from methyl borate by the action of zinc methyl (Frankland and Duppa, Annalen, 124, 129); has an intensely disagreeable smell, ignites spontaneously in the air; can be liquefied by a pressure of three atmospheres at 10°. Caustic potash absorbs the gas and yields, on evaporation, a viscid residue of $B(CH_3)_3·KOH$. Ammonia forms a compound $B(CH_3)_3·NH_3$, which can be crystallised from ether in large crystals; m.p. 56°; b.p. 110°.

Methyl bromide CH_3Br, *bromomethane*; b.p. 4·5° (corr.) (Perkin, Chem. Soc. Trans. 1884, 454); sp.gr. 1·73306 at 0·8°/0·8°.

Preparation.—By heating the cacodyl compound $As(CH_3)_2(OH)_2Br$ (Bunsen, Annalen, 46, 44); from methyl alcohol, bromine, and phosphorus (Pierre, Ann. Chim. [iii.] 15, 373). 133 grams red phosphorus, 800 grams methyl alcohol, are mixed in a retort, the mixture heated to the boiling-point, and 800 grams of bromine are gradually added; after some hours the mixture is distilled (Merrill, J. pr. Chem. [ii.] 18, 293; Steinkopf and Schwen, J. prakt. Chem. 1921, 102, 363). By dropping methyl sulphate into hydrobromic acid at 45°-50°, or better into a concentrated solution of an alkali bromide slightly acidified with sulphuric acid, at 30°–35° (Boulin and Simon, Compt. rend. 1920, 170, 595). By the action of hydrogen bromide, or potassium bromide and sulphuric acid, on methyl alcohol (Taboury, Bull. Soc. chim. 1911, [iv.] 9, 124; Bygden, J. pr. Chem. 1911, [ii.] 83, 421).

Methyl bromide is a colourless mobile liquid with a smell resembling that of chloroform, unites with water to form a crystalline hydrate $CH_3Br,20H_2O$ (?) which is decomposed at 4° (Merrill).

For brominated compounds of methyl bromide, *v. Methylene bromide*, art. Bromoform; and *Carbon tetrabromide*, art. Carbon.

Methyl chloride CH_3Cl, *chloromethane*; b.p. −23·73° (Regnault); −21° (Berthelot); −23° (Vincent and Delachanal); sp.gr. 0·99145 at −23°; 0·95231 at 0° (Vincent and Delachanal, Bull. Soc. chim. [ii.] 31, 11). Vap. press. at 0°=2·48 atmospheres, at 15°=4·11, at 30°=6·50 (Vincent and Delachanal). For compressibility, *see* Bodareu, Atti R. Accad. Lincei, 1914, [v.] 1, 491.

Preparation.—From methyl alcohol, common salt and sulphuric acid (Dumas and Peligot, Annalen, 15, 17); from methane and chlorine (Berthelot, Ann. Chim. [iii.] 52, 97); by heating the cacodyl compounds $As(CH_3)_2(OH)_2Cl$ or $As(CH_3)_2Cl$ (Bunsen, Annalen, 46, 44).

On the large scale by the dry distillation of 'vinasses' from beetroot. The methylamine is saturated with hydrochloric acid and concentrated, then heated to 260°-300°, when methyl chloride together with mono- and trimethylamine is evolved; the bases are removed by means of hydrochloric acid and the methyl chloride dried over calcium chloride and condensed by pressure in wrought-iron cylinders (Vincent and Delachanal, Bull. Soc. chim. [ii.] 31, 11; J. 1878, 1135). One part of melted zinc chloride is dissolved in two parts methyl alcohol and hydrogen chloride led into the mixture (Groves, Chem. Soc. Trans. 1874, 641).

Methyl chloride is obtained from methane by the action of carbonyl chloride at high temperatures:

$$CH_4+COCl_2=CH_3Cl+CO+HCl$$

The mixed gases which should contain a slight excess of methane are led over a catalyst capable of acting as a chlorine carrier or of accelerating the reaction by surface condensation (Hochstetter, D. R. P. 292089; J. Soc. Chem. Ind. 1916, 35, 867).

It may also be obtained by heating methyl sulphate with stannic chloride. At low temperatures the substances react with the intermediate formation of the methosulphate of stannyl chloride:

$$SnCl_4+2Me_2SO_4=2MeCl+SnCl_2(SO_4Me)_2$$

a white amorphous solid, decomposed at higher temperatures, giving stannic sulphate and methyl chloride (Boulin and Simon, Compt. rend. 1919, 169, 618).

It may also be prepared by dropping methyl sulphate into hydrochloric acid (D. 1·112) at about 50°:

$$Me_2SO_4+HCl=MeHSO_4+MeCl$$

(Boulin and Simon, *ibid.* 1920, 170, 595).

For observations on the chlorination of methane, *v.* Pfeifer, Mauthner, and Reitlinger, J. pr Chem. 1919, [ii.] 99, 239.

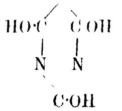
Properties.—Methyl chloride is a colourless gas with ethereal odour, and burns, when ignited in air, with a greenish flame. One part of water dissolves 4 volumes of methyl chloride; 1 of absolute alcohol, 35 volumes; and 1 of acetic acid, 40 volumes (Berthelot). The neutral solution is not precipitated by silver nitrate. With water at temperatures below 7·3° at 760 mm. it forms a solid hydrate $CH_3Cl,6H_2O$ (de Forcrand and Villard, Compt. rend. 106, 1402; Villard, Ann. Chim. [vii.] 11, 377). With chlorine in sunlight it yields methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and finally carbon tetrachloride CCl_4 (*q.v.* art. CARBON); the chlorination can also be effected by leading a mixture of chlorine and methyl chloride over animal charcoal at 250°-350°.

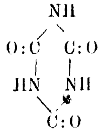
Methyl chloride forms with bromine methylene bromide, bromoform and carbon tetrabromide (Damoiseau, J. 1881, 376).

Methyl chloride is extensively used in the preparation of various coal-tar colours and also as a means of producing cold. By its evaporation a temperature of −23° is produced, or if the evaporation be accelerated by blowing in air −55° is easily reached, and since its vapour is non-poisonous, its superiority to liquid sulphur dioxide for this purpose is evident.

Methyl *iso*cyanate $CH_3{\cdot}N:CO$, *methyl carbimide*; b.p. 43°-45° (Gautier, Annalen, 1497, 313). Formed by the distillation of a mixture of 1 part of potassium cyanate with 2 parts of potassium methyl sulphate (Wurtz, Ann. Chim. [iii.] 42, 43); also by the action of diazomethane on nitro-urea (Degner and von Pechmann, Ber. 1897, 649). A liquid with intensely suffocating smell, converted by dry ammonia into methyl-urea $NH(CH_3)CO{\cdot}NH_2$ which forms prisms soluble in water. Water converts it into dimethyl-urea $NH(CH_3)CO{\cdot}NHCH_3$ with evolution of carbon dioxide.

Methyl cyanurates. Monomethyl, dimethyl, and trimethyl derivatives of both normal (I.) and *iso*cyanuric (II.) acids are known.


I.


II.

Normal trimethyl cyanurate $(NCOCH_3)_3$ is prepared from sodium methoxide and cyanogen chloride (Hofmann and Olshausen, Ber. 1870, 271). From dry sodium methoxide and cyanogen bromide (Ponomarew, *ibid.* 1885, 3264; Klason, J. pr. Chem. [ii.] 33, 131). Soluble in ether and water and crystallises in trimetric prisms melting at 135° and boiling at 265°. On long boiling it changes into the isomeride, melting at 175° (trimethyl *iso*cyanurate).

Normal dimethyl cyanurate $C_3N_3(OH)(OC_3H)_2$ results by heating 2 grams sodium in 15 grams absolute methyl alcohol and 15 grams normal trimethyl cyanurate to 100° for 1½ hours and decomposing the sodium salt with acetic acid (Hofmann, Ber 1886, 2067). It forms small six-sided leaves soluble in alcohol and water but not ether. It softens at 165°-170° and decomposes on further heating into dimethyl *iso*cyanurate, m p. 222°, and also trimethyl *iso*cyanurate, m.p. 175°.

Trimethyl isocyanurate $C_3O_3N_3(CH)_3$ is produced together with the normal trimethyl ester from silver cyanurate and methyl iodide (Ponomarew, Ber. 1885, 3271); also from the silver salt of the dimethyl derivative and methyl iodide (Hofmann, *ibid.* 1886, 2096); also by the interaction of cyanuric acid and diazomethane (Palazzo and Scelsi, Gazz. chim. ital. 1908, 38, i. 659). Monoclinic prisms melting at 175°-176° and boiling at 274°. Soluble in alcohol but not in water.

Dimethyl isocyanurate $(CH_3)_2H(CNO)_3$ is obtained by the dry distillation of methyl acetyl urea (Hofmann, Ber. 1881, 2069); also from the normal dimethyl derivative (*v. supra*). Monoclinic, thin leaves from water melting at 222°.

Monomethyl isocyanurate

$$(CH_3)H_2N_3C_3O_3,H_2O$$

is prepared by heating nitrosocarbonyldimethylurea with water (Fischer and Frank, Ber. 1897, 2615). It forms thin leaves, readily dehydrated at 100°, melting at 296°-297°, and has an unpleasant odour. On methylation the trimethyl derivative is produced.

Mixed derivatives have been prepared by Hantzsch and Bauer (Ber. 1905, 38, 1005). The di-o-mono-N- derivative, m.p. 105°, is prepared by the interaction of silver cyanate and methyl iodide below 0°. The mono-o-di-N- derivative, m.p. 118°, is prepared from silver cyanurate and methyl iodide at low temperatures.

Methyl cyanide $CH_3\cdot CN$, *acetonitrile*; b.p. 81·6°; sp.gr. 0·8052 at 0°, 0·7891 at 15° (Vincent and Delachanal, Bull. Soc. chim [ii.] 33, 405). H.C. at 18°=312·14 (Thomsen, Th. 4, 128) =291·6 (Berthelot and Petit, Compt. rend. 108, 1217).

From ammonium acetate and phosphorus pentoxide (Dumas, Compt. rend. 25, 383), from acetamide and phosphorus pentoxide; by distillation of potassium methyl sulphate with potassium cyanide (Dumas, Malaguti, and Leblanc, Annalen, 64, 333); in heating cyanacetic acid at 165° (Van 't Hoff, Ber. 1874, 1382); also by heating dimethyl sulphate with potassium cyanide (Walden, Ber. 40, 3214); by passing vapour of anhydrous acetic acid mixed with ammonia through a tube filled with pumice containing a deposit of alumina and heated to 500°. It is also formed by the action of prussic acid on diazomethane (von Pechmann, *ibid.* 1895, 857); and by pouring acetic acid over magnesium nitride (Emmerling, *ibid.* 1896, 1635).

Preparation.—A mixture of 5 molecules of acetamide and 1 molecule of phosphorus pentasulphide is distilled, the product washed with caustic soda and digested with lead oxide (Henry, Annalen, 152, 149). By long heating of a mixture of acetamide and glacial acetic acid under a reflux condenser (Demarçay, Bull. Soc. chim. [ii.] 33, 456).

Acetonitrile is a colourless liquid with a pleasant ethereal smell, miscible with water, from which it separates on the addition of common salt. It burns in air with a peach-blossom flame; with acetic acid at 200° it produces diacetamide. It is miscible with methyl alcohol or with ethyl alcohol, and its b.p. is lowered by such admixture—a liquid containing 80 p.c. wood spirit and 20 p.c. acetonitrile has the lowest b.p. (63·7°), whilst, in the case of ethyl alcohol, a mixture of 56 p.c. spirits of wine and 44 p.c. acetonitrile boils at 72·6° (Vincent and Delachanal, Bull. Soc. chim [ii.] 33, 405). It combines easily with dry hydrobromic or hydriodic acids, more difficultly with hydrochloric acid (Gautier, Annalen, 142, 291); by passing hydrogen chloride into a cooled mixture of acetonitrile and acetic acid, acetyl chloride and acetamide result (Colson, Bull. Soc. chim. [iii.] 17, 57). $CH_3CN\cdot 2HBr$ forms crystals melting at 47°–50° (Engler, Annalen, 149, 306). Bromine combines with acetonitrile at 100° to form a compound—$CH_2Br\cdot CN\cdot HBr$—crystallising in prisms which melt at 65°, and are decomposed by moist air, forming ammonium bromide, acetic acid, and dibromodiacetamide (Engler, Annalen, 133, 137; 142, 69). Sulphur trioxide produces the compound $(CH_3CN)_3 2SO_3$, which crystallises and dissolves in water, but not in organic solvents. By precipitating its aqueous solution with alcohol and ether crystals of the composition $(CH_3CN)_4(SO_3)_2.H_2O$ are obtained (Eitner, Ber. 1893, 2834).

By the action of sodium upon methyl cyanide, methane and an oily substance $C_4H_6N_2$ soluble in ether (Holtzwart, J. pr. Chem. [ii.] 38, 343), sodium cyanide, and *cyanmethine* $C_6H_9N_3$ are obtained (Baeyer, Ber. 1869, 319). This is best obtained by heating 6 parts methyl cyanide with 1 part of sodium under a pressure of 100 mm., distilling off the excess of methyl cyanide and crystallising the residue from alcohol (Meyer, J. pr. Chem. [ii.] 27, 153). It forms monoclinic crystals (m.p. 180°–181°), which dissolve in 0·64 part of water or 5·25 parts of alcohol at 18°. Cyanmethine unites with many acids, *e.g.* $C_6H_9N_3$.HCl, needles soluble in water; b.p. 200°–250° $(C_6H_9N_3)_2H_2SO_4$, crystallises with difficulty. It also forms chlorine and bromine derivatives (Baeyer, Ber. 4, 176). Treated with aluminium and cold sodium hydroxide solution (15 p.c.) acetonitrile gives a 75 p.c. yield of ethylamine (Ferrer, Anal. Fis. Quim. 1914, 12, 239).

Substitution products of acetonitrile.

Chloracetonitrile $CH_2Cl\cdot CN$, from chloracetamide and phosphorus pentoxide (Bisschopinck, Ber. 6, 732); the reaction is better carried out in a vacuum (Scholl, *ibid.* 1896, 2417). A liquid; b.p. 123°–124°, sp.gr. 1·204 at 11·2°, 1·193 at 20° (Engler, *ibid.* 1873, 1003).

Dichloracetonitrile $CHCl_2\cdot CN$; b.p. 112°–113°; sp.gr. 1·374 at 11·4° (Bisschopinck, Ber. 6, 732).

Trichloracetonitrile $CCl_3\cdot CN$; b.p. 83°–84°, sp.gr. 1·439 at 12·2°. From trichloracetamide and phosphorus pentoxide (Bisschopinck, Ber. 6, 732). By action of chlorine upon acetonitrile in presence of iodine (Beckurts, *ibid.* 1876, 1594).

Bromacetonitrile $CH_2Br\cdot CN$, and *dibromacetonitrile* $CHBr_2\cdot CN$, m.p. 142°, are also known (*v.* Engler, Annalen, 142, 69, and Van 't Hoff, Ber. 1874, 1571; also Henry, Compt. rend. 103, 413).

Iodacetonitrile $CH_2I\cdot CN$; b.p. 186°–187°; sp.gr. 2·3065 at 12°; from chloracetonitrile and sodium iodide in alcoholic solution (Henry, Compt. rend. 103, 413).

Nitroacetonitrile $CH_2(NO_2)CN$ *v.* FULMINIC ACID.

Dinitroacetonitrile $CH(NO_2)_2CN$, a syrupy liquid obtained by the action of sulphuric acid upon the ammonia compound $CH(NO_2)_2CN\cdot NH_3$: This compound is obtained by the reduction of an ethereal solution of trinitroacetonitrile by means of dry sulphuretted hydrogen:

$$C(NO_2)_3CN+4H_2S \\ \qquad CH(NO_2)_2CN\cdot NH_3+2H_2O+4S$$

(Schischkoff, Annalen, 101, 215; 119, 249; 104, 250).

Trinitroacetonitrile $C(NO_2)_3CN$, a solid, m.p. 41·5°; explodes when heated to 220°. Formed by the action of a mixture of fuming nitric and sulphuric acids upon sodium fulminate (Schischkoff, Ann. Chim. [iii.] 49, 310). Soluble in ether, but decomposed by alcohol, water, or alkalis.

Methyl *iso***cyanide** $CH_3\cdot NC$, *iso-acetonitrile*, *methyl carbylamine*; b.p. 59·6°; sp.gr. 0·7557 at 14° (Gautier, Annalen, 152, 222). From methyl iodide and 2 molecules of silver cyanide at 130° (Gautier, Compt. rend. 65, 468); also from chloroform, methylamine, and alcoholic potash (Hofmann). It is also formed in small quantity when potassium methyl sulphate is distilled with potassium cyanide.

Methyl *iso*cyanide is a liquid with a very unpleasant smell; soluble in 10 parts of water at 15°; forms crystalline salts with acids.

Methyl fluoride CH_2F. A gas, sp.gr. (H=1) 17·38, calc.=17·05 (Collie, Chem. Soc. Trans. 1889, 110). Obtained from potassium methyl sulphate and potassium fluoride (Dumas and Péligot, Annalen, 15, 59); by the action of heat upon tetramethyl ammonium fluoride (Collie); from a mixture of methyl iodide and silver fluoride (Moissan and Meslans, Compt. rend. 107, 1153; Chem. Soc. Trans. 1889, 364). Liquefied by a pressure of 30 atmospheres at ordinary temperatures; slightly soluble in water, more so in methyl alcohol It is very stable; critical temp. 44·9°; pressure 47123 mm. (Collie). For the physical constants of methyl fluoride, *see* Moles and Batuecas, J. Chim. Phys. 1919, 17, 537. Chlorine in sunlight displaces hydrogen and forms CH_2ClF, a gas soluble in water and of sp.gr. 34·18 (calc.=34·25).

Methyl formamide $H{\cdot}CO{\cdot}NH(CH_3)$; b.p. 180°–185° (Gautier, J. 1869, 618); 190° (Linnemann, J. 1869, 601); sp.gr. 1·011 at 19°. A thick oily liquid soluble in water and alcohol, insoluble in ether, formed by the distillation of methylamine formate.

Methyl formate $H{\cdot}CO{\cdot}OCH_3$; b.p. 32°–32·5° (corr.) (Perkin, Chem. Soc. Trans. 1884, 491); Volhard, Annalen, 176, 133). Sp.gr. 0·98239 at 15°/15°.

Preparation.—130 parts of methyl alcohol saturated with hydrogen chloride are gradually poured upon 100 parts of calcium formate; the mixture is then digested for some time, and finally distilled (Volhard, Annalen, 176, 133). A mixture of equivalent proportions of sodium formate, hydrochloric acid, and wood spirit may be used (Bardy and Bordet, Ann. Chim. [v.] 16, 561). Wood spirit is digested with formic acid, sp.gr. 1·22, and distilled, the distillate is then dehydrated by means of phosphorus pentoxide.

Methyl formate is a colourless liquid with a characteristic smell; its vapour is decomposed at a red heat, forming carbon monoxide and methyl alcohol. Chlorine in presence of sunlight yields *trichloro-methyl chloroformate* $Cl{\cdot}CO{\cdot}OCCl_3$, b.p. 127·5°–128°, sp.gr. 1·6525 at 14°, which, when heated at 340°–350°, yields carbonyl chloride $COCl_2$ (Hentschel, J. pr. Chem. [ii.] 36, 99). If the action be stopped at an earlier stage, a compound $C_4H_3Cl_5O_4$, b.p. 108°–109°, sp.gr. 1·4741 at 27°/27°, is formed. In the absence of sunlight, chloroformic ester $Cl{\cdot}COOCH_3$ is produced immediately (Hentschel, J. pr. Chem. [ii.] 36, 213; *cf.* Grignard, Rivat, and Ed. Urbain, Compt. rend. 1919, 169, 1074, and 1143).

Methyl-*cyclo*-hexanone *v. Ketones.*

Methyl hydrate *v. Methyl alcohol.*

Methyl hydride, Methane, *marsh gas*, CH_4; sp.gr. 0·559 (air=1); b.p. = −164·0° at 736·6 mm. (Olszewski, Ann. Chim. [ii.] 31, 58); sp.gr. of liquid=0·415 (O.); critical temp. 82·85; critical pressure, 45·6 atm.; critical density, 0·1623 (Cardoso). H.F.p.=21,750 cals.; H.F.v.=21,170 cals.; H.C.p. 2=11,930 cals. (Thomsen, Th. 4, 50): H.C.p.=213,500 cals. (Berthelot, Ann. Chim. [v.] 23, 179). 1 vol. of water at t° absorbs $0{\cdot}05449-0{\cdot}001807t+0{\cdot}0001028t^2$ vols. of marsh gas; 1 vol. of alcohol at t°, $0{\cdot}522586-0{\cdot}0028655t+0000142t^2$ vols. (Bunsen).

Marsh gas is emitted from the surface of the ground in many parts of the world, notably in Italy, North America, and in the vicinity of the Caspian Sea. It is formed by the putrefaction of vegetable matter under water, and hence occurs in marshy places. It is evolved in large quantities from the mud volcanoes of Sicily, Italy, and the Crimea. It also occurs in the coal measures, and, in small quantities, in the gases of the human intestines (Ruge, J. 1862, 528), and in the breath of calves and sheep (Reiset, J. 1863, 638).

It is formed by the putrefaction of cellulose. According to Hoppe Seyler, this is due to the action of a fungus (*Amylobacterium*. Van Tieghem, Compt. rend. 88, 205), and cellulose (sterilised filter-paper was used) is converted into a non-reducing sugar $C_6H_{12}O_6$, which splits up into $3CO_2$ and $3CH_4$; this action is stopped by a temperature above 60°.

Marsh gas is also produced by the destructive distillation of carbonaceous matter—*e.g.* wood or coal—and hence occurs, to the extent of about 40 p.c. by volume, in coal gas.

It can be obtained from chloroform or carbon tetrachloride by passing the vapour, mixed with hydrogen, through a hot tube, or by heating with copper, potassium iodide, and water (Berthelot, J. 1857, 267). Also by passing a mixture of the vapour of carbon disulphide and sulphuretted hydrogen over heated copper or iron (Berthelot, Ann. Chim. [iii.] 53, 69). Also by the action of the silent electrical discharge upon a mixture of hydrogen and carbon monoxide (Brodie, Proc. Roy. Soc. 21, 245), and by the direct combination of carbon and hydrogen at 1200° (Bone and Jerdan, Chem. Soc. Trans. 1897, 42; Bone and Coward, *ibid.* 1908, 1975), and also by the action of water on aluminium carbide (Moissan, Bull. Soc. chim. [iii.] 11, 1012; 15, 1285).

Carbon dioxide mixed with hydrogen is converted into methane when heated in presence of nickel as a catalyst:

$$CO_2+4H_2=CH_4+2H_2O$$

The reaction begins at 230°, and is rapid and nearly complete between 300° and 400°. By passing the product of the reaction through caustic soda, to free it from unchanged carbon dioxide, and condensing it by liquid air to free it from hydrogen, pure methane may be obtained.

It is also formed by the direct reduction of carbon monoxide by hydrogen in presence of nickel: $CO+3H_2=CH_4+H_2O$. The reaction begins at 180° and proceeds rapidly at 230°–250°. If the gases are mixed in theoretical proportions the methane is obtained almost pure. At temperatures above 250° part of the carbon monoxide is converted into carbon dioxide and carbon: $2CO\rightleftarrows C+CO_2$, owing to the specific action of the nickel at these temperatures.

This last is a simple method of obtaining methane free from admixed gases. For details, *see* Harger, Colliery Guardian, March, 1913; Campbell and Parker, Chem. Soc. Trans. 1913, 103, 1292.

These methods of preparing an industrial gas rich in methane, of high calorific power, and suitable for incandescent lighting, have been covered by patents. *See* Henderson's Catalysis in Industrial Chemistry, Longmans.

Preparation.—By heating potassium acetate with caustic potash

$$KC_2H_3O_2+KOH=K_2CO_3+CH_4$$

Sodium acetate and a mixture of equal volumes of calcined soda and powdered lime are heated in an iron or copper vessel (Schorlemmer, Chem. News, 29, 7), hydrogen and ethylene are also produced in this reaction (Kolbe); the latter may be removed by means of sulphuric acid.

It can also be obtained by the action of the copper-zinc couple upon a mixture of equal volumes of alcohol and methyl iodide (Gladstone and Tribe, Chem. Soc. Trans. 1884, 154). Methane is also obtained by the decomposition of zinc methyl with alcohol or water.

Properties.—Methane is colourless and odourless, and forms an explosive mixture with air ('firedamp'). In mixtures of methane and air containing from 5 to 9·2 p.c. of methane the decomposition is $CH_4+2O_2=CO_2+2H_2O$, but with larger quantities, in addition to carbon dioxide and water, hydrogen and carbon monoxide are formed. It is very stable, and is not affected by phosphorus pentoxide or antimony pentachloride, or even by strong nitric acid. Dry chlorine has no action in the dark, but in sunlight the mixture explodes; in diffused daylight chloro substitution derivatives are formed, viz. methyl chloride, methylene dichloride, chloroform, and carbon tetrachloride. For observations on the chlorination of methane, *v.* Pfeifer, Mauthner, and Reitlinger, J. pr. Chem. 1919, [ii.] 99, 239; Whiston, Chem. Soc. Trans. 1920, 183. When passed through a hot tube, a small portion is converted into naphthalene. At higher temperatures it is more or less dissociated in amount dependent on the temperature, and the amount and nature of the heated surface (Bone and Coward; Campbell and Slater). It is very gradually absorbed by cold fuming sulphuric acid (Worstall, J. Amer. Chem. Soc. 1899, 246). It may be oxidised to methyl alcohol and formaldehyde (*see Methyl alcohol*).

It forms a hydrate with water at −2° or 3° under a pressure of 30 atmospheres. Tension of dissociation at 0°−27·5 atmospheres; crit. temp.=21·5° (Villard, Compt. rend. 107, 295).

Methyl iodide CH_3I; b.p. 42·3° (corr.) (Perkin, Chem. Soc. Trans. 1884, 459); 42·9° (corr.) (Thorpe and Rodger, Phil. Trans. 1894, A. 11, 464); sp.gr. 2·28517 at 15°/15° (P.); 2·2677 at 15° (Bardy and Bordet, Ann. Chim. [v.] 16, 569). Formed by the action of phosphorus and iodine upon methyl alcohol (Dumas and Péligot, Annalen, 15, 30).

Preparation.—In a similar manner to that of ethyl iodide (*q.v.*). 35 parts methyl alcohol, 100 parts iodine, and 10 parts of phosphorus are the proportions usually employed. These substances are allowed to remain in contact for some hours; the methyl iodide is then distilled off, washed with dilute caustic soda solution, and dried by means of calcium chloride. The preparation from an iodide of an alkali or alkaline earth by the action of methyl sulphate is patented by Weinland and Schmidt (D. R. P. 175209, 1905). A yield of 94 p.c. is obtained by dissolving yellow phosphorus in methyl iodide, and adding iodine to the liquid, and slowly dropping methyl alcohol into the cooled mixture (Walker and Johnson, Chem. Soc. Trans. 1905, 1595).

It forms a colourless liquid which turns brown on exposure to light owing to the liberation of iodine. It is extensively used in the preparation of various aniline colours owing to the ease with which it undergoes decomposition; it thus affords a ready means of introducing the methyl group into other compounds.

Methyl nitrate CH_3NO_3; b.p. 65°; sp.gr. 1·2167 at 15°/15° (Perkin, Chem. Soc. Trans. 1884, 682).

Preparation.—200 c.c. pure wood spirit are distilled with 40 grams urea nitrate and 150 c.c. pure nitric acid (sp.gr. 1·31) until two-thirds have distilled off; to the residue 170 c.c. of methyl alcohol and 130 c.c. nitric acid are added, again distilled, and then 150 c.c. methyl alcohol, 110 c.c. nitric acid, and 10 grams urea nitrate are added to the residue, and distillation again continued (C. Lea, J. 1862, 387).

Can also be prepared by mixing methyl alcohol and sulphuric acid, and adding 2 parts of this liquid to a mixture of 1 part nitric acid and 2 parts sulphuric acid. The distillate is washed with potassium carbonate solution. Delépine recommends the following: A mixture of 50 c.c. strong sulphuric acid and 150 c.c. methyl alcohol cooled to 12° are carefully added to a mixture of 100 c.c. strong sulphuric acid and 150 c.c. nitric acid (36°), cooled to 12°, so that the temperature does not rise above 15°. Afterwards the whole is shaken with 100 c.c. strong sulphuric acid. After a few minutes' standing the ester is separated off (Bull. Soc. chim. [iii.] 13, 1044).

Methyl nitrate is a colourless liquid with a pleasant smell; explodes when heated to 150°, or by percussion.

Methyl nitrite CH_3NO_2; b.p. −12°; sp.gr. of liquid 0·991 at 15°/. A gas, prepared by treating 1 molecule methyl alcohol with 1 molecule *iso*amyl nitrite (Bertoni, Gazz. chim. ital. 12, 438). Also by the action of nitric acid upon copper (or arsenious acid) and methyl alcohol, or by the action of nitric acid upon brucine (Strecker, Annalen, 91, 76).

Methyl oxalate $(CH_3)_2C_2O_4$; m.p. 54°; b.p. 163·3° (corr.) (Weger, Annalen, 221, 86). Oxalic acid (dried at 100°) is mixed with boiling methyl alcohol, and on cooling the crystals separate out (Erlenmeyer, J. 1874, 572).

Forms monoclinic plates, which, by action of chlorine yield, first, an oily liquid of the composition $C_2O_4(CHCl_2)_2$ (Malaguti, Annalen, **32**, 49), and by prolonged action in sunlight, a body $C_2O_4(CCl_3)_2$, which crystallises in leaflets (Cahours, *ibid.* 64, 313).

Methyl hydrogen oxalate $H(CH_3)C_2O_4$. When oxalic ethyl ester is treated in methyl alcoholic solution with potassium methoxide, potassium methyl oxalate is thrown out in the form of fine leaves (Salomon, Ber. 8, 1509). Methyl hydrogen oxalate is a solid of low melting-point which boils at 108°–109°/ 12 mm. (Anschütz and Schonfeld, Ber. 19, 1442).

Methyl oxide, Dimethyl ether $(CH_3)_2O$; b.p. −23·65° (Regnault, J. 1863, 70); −21° (Berthelot); sp.gr. (air=1) 1·617.

Formed by heating methyl alcohol with sulphuric acid (Dumas and Péligot, Ann. Chim. [ii.] 58, 19), or with boron trioxide (Ebelmen, *ibid.* [iii.] 16, 138; Annalen, 57, 328).

1·3 parts of wood alcohol are mixed with 2 parts of sulphuric acid, and heated to 140°. The gas evolved is passed into strong sulphuric acid, which absorbs 600 times its volume; the gas is then set free by diluting the acid with an equal volume of water (Erlenmeyer and Kriechbaumer, Ber. 1874, 699).

Methyl ether is a colourless gas with a pleasant odour; 1 vol. of water at 18° absorbs 37 volumes of the gas (Dumas and Péligot). It unites with hydrochloric acid to form a compound $(CH_3)_2O{\cdot}HCl$, which boils at 2° (Friedel, Bull. Soc. chim. [ii.] 24, 160, 241).

Chlorine Substitution Products.

Chloromethyl ether $CH_2Cl{\cdot}O{\cdot}CH_3$; b.p. 59·5° at 759 mm.; formed by bringing together, in diffused daylight, chlorine and excess of methyl oxide (Friedel, Bull. Soc. chim. [ii.] 28, 171). It is decomposed by water into hydrochloric acid, trioxymethylene $(CH_2O)_3$, and methyl alcohol.

Dichloromethyl ether $(CH_2Cl)_2O$; b.p. 105°; sp.gr. 1·315 at 20°; formed by the action of chlorine upon methyl oxide (Regnault, Annalen, 34, 31).

Tetrachloromethyl ether $(CHCl_2)_2O$; b.p. 130°; sp.gr. 1·606 at 20° (Regnault).

Perchloromethyl ether $(CCl_3)_2O$; b.p. 100° (with decomposition); sp.gr. = 1·597; by the action of chlorine upon methyl oxide in sunlight (Regnault). Decomposed by heat, yielding carbon tetrachloride and carbonyl chloride. (*See also* de Sonay, Ber. 1894, Ref. 337.)

Methyl phosphates.

1. *Normal methyl phosphate* $(CH_3)_3PO_4$; b.p. 197·2° (corr.); sp.gr. 1·2378 at 0° (Weger, Annalen, 221, 89). From methyl iodide and silver phosphate (Hall, Chem. Soc. Trans. 51, 751).

2. *Dimethyl phosphoric acid* $(CH_3)_2HPO_4$; a syrupy liquid, produced when phosphoryl chloride $POCl_3$ is dropped into methyl alcohol (Schiff, Annalen, 102, 234). The salts are very soluble in water.

3. *Monomethyl phosphoric acid* $CH_3H_2PO_4$ is produced when methyl alcohol is dropped into phosphoryl chloride (Schiff, Annalen, 102, 337).

Methyl phosphites.

Monomethyl phosphite $CH_3H_2PO_3$, a syrupy liquid formed by the action of phosphorus trichloride upon methyl alcohol (Schiff, Annalen, 103, 164). It is miscible with ether, and forms salts which are amorphous, and are decomposed by water into methyl alcohol and phosphites.

Trimethyl phosphite $P(OCH_3)_3$ is a liquid boiling with partial decomposition at 185°. It is prepared by the action of phosphorus trichloride on sodium methoxide. Sp.gr. 1·1785 at 15° (Jaehne, Annalen, 256, 281).

Methyl salicylate $C_6H_4(OH){\cdot}COO{\cdot}CH_3$. Is the chief constituent of oil of winter-green. Obtained by distilling a mixture of salicylic acid, methyl alcohol, and sulphuric acid. B.p. 222·2°; sp.gr. 1·189 at 15°/15°. Used in perfumery and pharmacy.

Methyl sulphates.

1. *Hydrogen methyl sulphate, methyl sulphuric acid* CH_3HSO_4. The free acid is an oily body, which remains liquid at −30°. Obtained from methyl alcohol and sulphuric acid (Dumas and Péligot, Annalen, 15, 40), or from methyl alcohol and chlorosulphonic acid in the cold (Claesson, J. pr. Chem. [ii.] 19, 240).

Preparation.—One part of methyl alcohol is mixed with two parts of concentrated sulphuric acid, allowed to stand in a warm place for some hours, diluted with water and neutralised with barium carbonate, filtered and the barium precipitated by the proper quantity of sulphuric acid. Methyl sulphuric acid forms salts with the metals, which are soluble and readily crystallise. On distillation it decomposes into dimethyl sulphate and sulphuric acid (Claesson).

Chloride of methyl sulphuric acid CH_3SO_3Cl. *Methyl chlorosulphonate* is obtained by dropping methyl alcohol into sulphuryl chloride in molecular proportions (Behrend, J. pr. Chem. [ii.] 15, 32), or by passing sulphur dioxide into methyl hypochlorite (Sandmeyer, Ber. 1886, 861), or by the action of chlorosulphonic acid on methyl hydrogen sulphate or on methyl sulphate (Levaillant and Simon, Compt. rend. 1919, 169, 140–234). It is an oily liquid with pungent smell; decomposed by water into methyl sulphuric and hydrochloric acids.

The same products may be obtained by treating methyl alcohol with sulphur dioxide and chlorine in the proportion of 1 molecule of each of the gases to 2 molecules of the alcohol (Boake and Durrans, Eng. Pat. 119250). Methyl chlorosulphonate boils at 42°/16 mm., 134°–135°/760 mm; D^{15} 1·492; n_D^{17} 1·414.

2. *Dimethyl sulphate* $(CH_3)_2SO_4$; b.p. 188°; sp.gr. 1·33344 at 15° (Perkin, Chem. Soc. Trans. 1886, 785). By distilling wood spirit with 8 or 10 parts of sulphuric acid (Dumas and Péligot, Ann. Chim. [ii.] 58, 54) or by distilling anhydrous methyl sulphuric acid, best *in vacuô* (Claesson, J. pr. Chem. [ii.] 19, 244). Methyl sulphate is prepared by bringing together methyl alcohol (27 grams) and chlorosulphonic acid (100 grams) at −10° and then distilling the mixture under 20 mm. pressure at 140°. The yield is 80–83 p.c. theoretical. Fuming sulphuric acid gives a yield of only 42 p.c. (D. R. P. 113239). By adding 4 parts of 60 p.c. oleum to 1 part of methyl alcohol cooled to −18° and subsequently distilling the mixture under reduced pressure, a yield of 90 p.c. of the theoretical amount is obtained. The Société Anonyme des Produits Chimiques de Fontaines in Lyon-Monplaisir uses practically the same process with carbon tetrachloride as a diluent (D. R. P. 193830). By treating cooled methyl alcohol with chlorine and sulphur dioxide (Durrans, U.S. Pat. 1317648). Haworth and Irvine (Eng. Pat. 122498) combine dry dimethyl ether and sulphur trioxide in presence of a solvent which may conveniently consist of methyl sulphate itself. The yield of dimethyl sulphate by the action of sulphuric acid on methyl alcohol increases within limits with increase in the molecular proportion of sulphuric acid. The complete reaction appears to be a balance of three reactions:

$$H_2SO_4 + CH_3{\cdot}OH \rightleftarrows CH_3{\cdot}HSO_4 + H_2O$$

$$2CH_3{\cdot}HSO_4 \rightleftarrows H_2SO_4 + (CH_3)_2SO_4$$

$$CH_3{\cdot}HSO_4 + CH_3{\cdot}OH = H_2SO_4 + (CH_3)_2O$$

In order to obtain the best yield of dimethyl sulphate it is necessary to avoid the presence of water or of excess of methyl alcohol (Guyot and Simon, Compt. rend. 1919, 169, 655). It is extensively used as a methylating agent for aromatic amines, the reaction being:

$$Me_2SO_4+2R\cdot NH_2=RNH_2\cdot MeHSO_4+R\cdot NHMe$$

(Ullmann, Annalen, 327, 103). *cf.* however, Claesson and Lundvall (Ber. 13, 1699). Quinoline and quinaldine are both quantitatively converted into their ammonium bases by treatment with methyl sulphate in benzene solution (Ullmann, *l.c.*). It is also a very convenient reagent for esterifying acids (Carl Graebe, *ibid.* 344, 244). On distillation under reduced pressure of the products obtained by the action of methyl sulphate on alcoholic solutions of sodium penta-, tetra-, or tri-sulphide *methyl trisulphide*, Me_2S_3, has been obtained by Strecker (Ber. 1908, 1105. *Cp.* also Klason, Chem. Soc. Abstr. 1888, 356). A colourless liquid with an odour like that of peppermint.

Methyl sulphides.

1. *Hydrogen methyl sulphide, methyl mercaptan, methyl sulphydrate*, CH_3SH (Gregory, Annalen, 15, 239); b.p. 5·8° at 752 mm. (Klason, Ber. 20, 3407); a°=0·894. By heating potassium hydrogen sulphide with potassium methyl sulphate (Dumas and Péligot), or by acting upon *s*-methyl-*iso* thiocarbamide sulphate (prepared by warming an aqueous solution of thiocarbamide with methyl sulphate) with dilute sodium hydroxide solution, when it is converted into cyanamide and methyl mercaptan (Arndt, Ber. 1921, 54, B, 2236). It is a colourless liquid with a disagreeable odour and forms a crystalline hydrate with water. By the action of chlorine upon carbon disulphide containing a little iodine, *Perchloromethyl mercaptan* CCl_3ClS, a liquid (b.p. 146°–148° corr.; sp.gr. 0° 1·712 at 12·8°) is obtained (Rathke, Annalen, 167, 195). This substance is decomposed by heating to 200° into carbon tetrachloride and sulphur chloride.

2. *Dimethyl sulphide* $(CH_3)_2S$; b.p. 37·1°–37·3° at 754·7 mm. (Beckmann, J. pr. Chem. [ii.] 17, 453); b.p. 37·2° at 758 mm. (Klason, Ber. 20, 3407); 37·52° (corr.); sp.gr. 0·8702 at 0°/4° (Thorpe and Rodger). Sp.gr. 0·845 at 21° (Regnault, Annalen, 34, 26). From potassium sulphide and methyl chloride (Regnault, Ann. Chim. [ii.] 71, 391).

Preparation.—500 c.c. methyl alcohol are treated with 750 c.c. sulphuric acid, and a solution of 2·75 kilos. sodium carbonate (crystals) is added, and the solution concentrated until the sodium sulphate crystallises out. To the solution of sodium methyl sulphate 500 grams of potash dissolved in water and half saturated with sulphuretted hydrogen are added. The yield is about 150 grams (Klason, Ber. 1887, 3407; Chem. Soc. Trans. 1888, 356). Methyl sulphide is a colourless liquid with an unpleasant smell. It combines directly with chlorine to form oily substitution products $(CH_2Cl)_2S$, $(CHCl_2)_2S$, and $(CCl_3)_2S$ (Riche, Ann. Chim. [iii.] 43, 283). Bromine unites with it to form a crystalline bromide $(CH_3)_2SBr_2$ (Cahours, Annalen, 135, 355). It also forms many crystalline compounds with various salts, *e.g.*

$$(CH_3)_2S\cdot HgCl_2$$

$2(CH_3)_2S\cdot PtCl_4$), &c. (Loir, Ann. Chim. [iii.] 39, 448; 54, 42). It combines at ordinary temperatures with methyl iodide to form *trimethyl sulphine iodide* $(CH_3)_3SI$, which crystallises in prisms.

By the action of moist silver oxide upon this compound there is formed *trimethyl sulphine hydroxide* $(CH_3)_3S\cdot OH$, an oily liquid which possesses strongly basic properties and forms characteristic salts with the acids. Sulphuretted hydrogen reacts with the base, yielding the *hydrosulphide* $[(CH_3)_3S]SH$, which on treating with one molecular proportion of the hydroxide yields the *normal sulphide* $[(CH_3)_3S]_2S$, which resembles in its reactions the sulphides of the alkalis (Brown and Blackie, Chem. News, 37, 130; 39, 51).

Methyl trisulphide $(CH_3)_2S_3$ has been prepared by Strecker (*see* above *Dimethyl sulphate*).

Methyl sulphite $(CH_3)_2SO_3$ or $SO(OCH_3)_2$; b.p. 121·5°; sp.gr. 1·0456 at 16·2°/4°. Obtained from methyl alcohol and sulphur chloride S_2Cl_2 (Carius, Annalen, 110, 209; 111, 96). Is isomeric with ethyl sulphurous acid $OH\cdot SO\cdot OC_2H_5$, and ethyl sulphonic acid $C_2H_5SO_2\cdot OH$.

Methyl chlorosulphinate $Cl\cdot SO_2\cdot CH_3$ is formed when well cooled methyl alcohol is mixed with thionyl chloride. It boils at 19°/13 mm. or 102°/755 mm. with decomposition into sulphur dioxide and methyl chloride. Is readily decomposed by water into sulphur dioxide, hydrogen chloride, and methyl alcohol (Stahler and Schirm, Ber. 1911, 44, 319).

Methyl sulphonic acid $CH_3SO_2\cdot OH$, a syrupy liquid decomposed at about 130°. By the action of nitric acid upon methyl thiocyanate or disulphide (Muspratt, Annalen, 65, 261). Also by heating methyl iodide with sodium sulphite solution to 120° (Collmann, *ibid.* 148, 105), and by the reduction of trichloromethane sulphonic acid (Kolbe, *ibid.* 54, 174), and also by the action of chloride of lime on methyl thiocyanate (de Coninck, Compt. rend. 126, 828). It forms stable crystalline salts which are very soluble in cold water but almost insoluble in alcohol. The potassium compound $CH_3\cdot SO_2\cdot OK$, is decomposed by heating with caustic potash—

$$CH_3\cdot SO_2OK+3KOH=3H_2+K_2CO_3+K_2SO_3$$

(Berthelot, J. 1869, 336).

For the reactions of *methyl disulphonic acid* (methionic acid), and its applications in syntheses, *see* Schroeter and collaborators (Annalen, 1919, 418, 161; Chem. Soc. Abstr. 1919, i. 516).

Methyl sulphonic chloride $CH_3\cdot SO_2Cl$; b.p. 150°–153° (Carius); 160° (Nithack); sp.gr. 1·51 (Gowan, J. pr. Chem. [ii.] 30, 281). By the action of phosphorus pentachloride upon methyl sulphonic acid (Carius, Annalen, 114, 142). It is not acted upon by sulphuretted hydrogen or potassium cyanide in alcoholic solution. Ammonia forms an amide

$$CH_3\cdot SO_2\cdot NH_2$$

which crystallises in long prisms (Gowan, *l.c.*, also Chem. Soc. Trans. 48, 367).

Chloromethyl sulphonic acid $CH_2Cl\cdot SO_2\cdot OH$, an acid syrup obtained by the action of nascent hydrogen upon trichloromethyl sulphonic acid (Kolbe, Annalen, 54, 168).

Dichloromethyl sulphonic acid $CHCl_2\cdot SO_2\cdot OH$, an unstable body formed by the action of zinc upon trichloromethyl sulphonic acid (Kolbe, Annalen, 54, 164); also by heating chloroform with a solution of potassium sulphite to 180° (Strecker, *ibid.* 148, 92). The *chloride*

$$CHCl_2{\cdot}SO_2Cl$$

(b.p. 170°–180°, sp.gr. 1·71) is formed by the action of phosphorus pentachloride upon the acid (Gowan, J. pr. Chem. [ii.] 30, 399), or by reducing, by means of sulphur dioxide or stannous chloride, trichloromethyl sulphonic chloride (Kolbe).

Trichloromethyl sulphonic acid

$$CCl_3{\cdot}SO_2{\cdot}OH,H_2O$$

m.p. 130°. The free acid is obtained from the chloride by treatment with baryta, and precipitation of the dissolved barium by means of sulphuric acid, the excess of sulphuric acid is then removed by means of lead carbonate and excess of lead by means of sulphuretted hydrogen (Gowan, J. pr. Chem. [ii.] 30, 284).

It forms small prisms which are very stable and insoluble in water, but soluble in alcohol or ether. It has strong acid properties and is not affected by nitric acid, aqua regia, or chromic trioxide.

Trichloromethyl sulphonic chloride $CCl_3{\cdot}SO_2Cl$ (m.p. 135°, b.p. 170°) forms camphorlike crystals, and is obtained by the action of moist chlorine upon carbon disulphide (Berzelius and Marcet, Gilbert's Annalen, 48, 161). Bassett (Chem. News, 54, 79) recommends the following process: 100 grams of powdered potassium chlorate, 200 c.c. hydrochloric acid, 400 c.c. water, and 50 c.c. carbon disulphide are mixed together and allowed to stand for some days until the carbon disulphide becomes solid; the white solid is then removed by filtration and washed; the yield is 63 grams. It is very stable and reacts with difficulty or not at all with aromatic amines. With secondary and tertiary organic bases it yields colouring matters. It also oxidises leuco bases and their sulphonic acids to colouring matters (Espenschied, D. R. P. 14621).

Methyl thiocyanate $CH_3{\cdot}S{\cdot}CN$; b.p. 132·9 at 757·2 mm.; sp.gr. 1·088 at 0° (Pierre, J. 1851, 51). H.C.=398·95 cals. (Thomsen, Th. 4, 196). By heating methyl sulphide with cyanogen bromide to 100° (Cahours, J. 1875, 257). By distilling a concentrated solution of equal parts of potassium thiocyanate and calcium methyl sulphate (Cahours, Annalen, 61, 95). Calcium methyl sulphate may be replaced with advantage by methyl sulphate in theoretical proportions.

If heated to 180°–185° it is partially converted into the *iso*thiocyanate. By the action of chlorine in daylight cyanuric chloride $Cl_3(CN)_3$, thiocarbonyl chloride $CSCl_2$, and thiocarbonyl tetrachloride $CSCl_4$ are obtained (James, Chem. Soc. Trans. 51, 272). By heating with methyl iodide to 100° trimethyl sulphine iodide $(CH_3)_3SI$ is produced (Cahours, J. 1875, 257).

Methyl *iso*thiocyanate $CH_3{\cdot}NCS$, *methyl mustard oil*; m.p. 34°; b.p. 119° (Hofmann, Ber. 1, 172). By heating the silver salt of methyl thiocarbamic acid $CS(NH{\cdot}CH_3)SH$ with water. This acid is formed by the action of carbon disulphide upon methylamine. Methyl mustard oil forms white crystals which have a smell resembling that of horse-radish.

Methyl selenide $(CH_3)_2Se$; b.p. 58·2°. Obtained by distilling a solution of sodium selenide (prepared from phosphorus pentaselenide and caustic soda) with potassium methyl sulphate (Jackson, Annalen, 179, 1). A disagreeably smelling liquid; with platinum tetrachloride forms a yellow compound $2(CH_3)_2Se{\cdot}PtCl_4$, soluble in alcohol. It also unites with chlorine and bromine $(CH_3)_2SeCl_2$, m.p. 59·5°; $(CH_3)_2SeBr_2$, m.p. 82°.

Methyl diselenide $(CH_3)_2Se_2$, a heavy, reddish yellow liquid with very unpleasant odour, formed when potassium diselenide is heated with potassium methyl sulphate (Wöhler and Dean, Annalen, 97, 5; Rathke, *ibid.* 152, 211).

Methylamines.

These are compounds with strongly marked basic properties, derived from ammonia by the replacement of one, two, or three atoms of hydrogen by an equal number of methyl groups.

Methylamine $(CH_3)NH_2$, *monomethylamine*; b.p. −6° to −5·5° at 768·35 mm.; crit. temp. 156·9°; crit. press. 73·6 atm. (Berthoud); sp.gr. 0·699 at −10·8° (Hofmann, Ber. 22, 699).

Occurrence.—In the oil yielded by the dry distillation of bone (Anderson, Annalen, 88, 44). In the plants *Mercurialis annua* (Linn.) and *M. perennis* (Linn.) (Reichardt, J. 1865, 457). In herring brine (Tollens, Zeitsch. Chem. 1866, 516) and in the products of the putrefaction of fish. In crude wood spirit (Commaille, J. 1873, 686; Vincent, Ann. Chim. [v.] 1, 444). In the products of the dry distillation of the residues from beet-sugar 'vinasses' (Duvillier and Buisine, Ann. Chim. [v.] 23, 317).

In the products of distillation of bran with lye (Laycock, Chem. News, 1898, 78, 210, 233). In the products yielded by the decomposition of fibrin by *streptococci* (Emmerling, Ber. 1897, 30, 1863).

Formation.—By the action of caustic potash upon methyl *iso*-cyanate or *iso*-cyanurate (Wurtz, Ann. Chim. [iii.] 30, 443). From ammonia and methyl iodide (Hofmann, Phil. Trans. 1851, 381) or methyl nitrate (C. Lea, Chem. News, 6, 46; Juncadella, Compt. rend. 48, 342). By heating wood spirit with sal ammoniac to 300° (Berthelot, Ann. Chim. [iii.] 38, 69).

If a solution of formaldehyde and ammonium chloride is heated, the former, whether present in excess or not, acts on the trimethylene triamine first formed and yields methylamine in theoretical quantity. If the ammonium chloride is in large excess, the amine is very pure; if the aldehyde is in large excess, trimethylamine is the final product (Plöchl, Ber. 21, 2117; Brocket and Cambier, Compt. rend. 1895, 120, 557; Eschweiler, Ber. 1905, 38, 880; Koeppen, Ber. 1905, 38, 882; Knudsen, Ber. 1914, 47, 2694; Werner, Chem. Soc. Trans. 1917, 111, 844; Jones and Wheatley, J. Amer. Chem. Soc. 1918, 40, 1411).

Chloropicrin treated with iron filings and acetic acid (Geisse, Ann. 1859, 109, 282) or tin and hydrochloric acid (Wallach, *ibid.* 1877, 184, 51) yields monomethylamine:

$$CCl_3{\cdot}NO_2+12H=CH_3{\cdot}NH_2+3HCl+2H_2O$$

(*cf.* Frankland, Challenger and Nicholls, Chem. Soc. Trans. 1919, 159).

Methylamines are produced by heating ammonium methyl sulphates at about 260°, when the yield of methylamine is about 27 p.c.

of the theoretical yield; when a mixture of ammonium methyl sulphate with two equivalents of ammonium benzene sulphonate is heated the yield of methylamine is about 50 p.c. of the theoretical amount (*cf.* Werner, Chem. Soc. Trans. 1914, 105, 2762; Denham and Knapp, *ibid.* 1920, 236). They are also formed by heating methyl alcohol under pressure with a mixture of ammonium chloride and zinc chloride. The yields are 55·0, 7·5, and 1·86 p.c. respectively of mono-, di-, and tri-methylamine, calculated on the weight of the ammonium chloride (Turner and Howard, J. Amer. Chem. Soc. 1920, 42, 2663).

By heating caustic potash with certain alkaloids—*e.g.* morphine, codeine, creatine, &c. (Wertheim, Annalen, 73, 210; Dessaignes, J. 1855, 331). By the action of chlorine upon caffeine or theobromine (Rochleder, J. 1850, 435). By the action of nascent hydrogen, from zinc and sulphuric acid, upon hydrocyanic acid (Mendius, Annalen, 121, 139). By passing a stream of hydrogen and hydrocyanic acid gas over platinum black, heated to 110° (Debus, Chem. Soc. Trans. 16, 249).

By the reduction of hexamethylenetetramine with zinc dust and hydrochloric acid (D. R. P. 73812); of formamide with sodium in amyl alcohol solution (Guerbet, Bull. Soc. chim. [iii.] 21, 780), or of nitromethane electrolytically in sulphuric acid solution at 70°-75° (Pierron, *ibid.* 783)

Preparation.—Equal molecules of methyl nitrate and ammonia dissolved in methyl alcohol are heated to 100°. The product is decomposed by caustic soda, and the base combined with hydrochloric acid, the dried chloride is then heated with caustic soda, and the liberated methylamine passed into sulphuric acid, the sulphate is dried at 110° and treated with absolute alcohol in which the di- and tri-methylamine salts are soluble; the insoluble monomethylamine sulphate is then decomposed by potash, and the free methylamine passed into a cooled solution of ethyl oxalate. The resulting di-methyl oxamide is dissolved in hot water, filtered and recrystallised, then decomposed by caustic potash, and the gas passed into absolute alcohol (Duvillier and Buisine, Ann. Chim. [v.] 23, 324; *v.* also Muller, Bull. Soc. chim. [ii.] 42, 202; Chem. Soc. Trans. 48, 501).

It can also be prepared by the interaction of acetamide and bromine in caustic potash solution (Hofmann, Ber. 1882, 15, 765; 1885, 18, 2741; François, Compt. rend. 1908, 147, 680): or by heating formaldehyde with ammonium chloride at 40°-95°.

Methylamine can be prepared electrolytically, cheaply and conveniently, according to the following process: An electrolytic cell, provided with a diaphragm separating the cathode and anode, is filled with a solution of sodium sulphate, and 140 grams hexamethylenetetramine is added. The electrolysis is carried out by means of lead electrodes and a current of 3 amperes per square decimetre. The alkali formed at the cathode is neutralised by the careful addition, drop by drop, of dilute sulphuric acid. The temperature must be kept at about 20°. Methylamine and trimethylamine are thus formed, and can be separated in the ordinary way. Ammonium sulphate can replace the sodium sulphate (D. R. P. 148054; Frdl. 1902–04, 26; *see also* D. R. P. 143197; Frdl. 1902–04, 25).

Commercial methyl sulphate is added in small portions at a time to excess of a 10 p.c. aqueous solution of ammonia at −5°. The product is then added to an excess of a 30 p.c. aqueous solution of sodium hydroxide, and the mixture is distilled, the issuing gas being collected in 20 p.c. hydrochloric acid. The methylamine hydrochloride is separated from the ammonium chloride by fractional crystallisation, and is finally purified by recrystallisation from alcohol (Burmann, Bull. Soc. chim. 1906, [iii.] 35, 801)

According to Bertheaume (*ibid.* 1908, 146, 1215) this method of separation is of very little use (Fleck, J. Amer. Chem. Soc. 1896, 18, 670).

A better method of separating the three amines than the one given above, is to treat the concentrated solution of their hydrochlorides with caustic soda and collect the gas evolved in formaldehyde. The liquid is now treated with an equal weight of caustic potash, whereby the greater part of the trimethylamine is evolved, whilst the methylene derivatives of mono- and di-methylamine remain in solution, and can be fractionated by distillation. The amines are regenerated by boiling the condensation products with alcoholic hydrochloric acid (Delépine, Compt. rend. 1896, 122, 1064; Ann. Chim. 1896, [vii.] 8, 439).

Methylamine may be separated from ammonia by shaking the aqueous mixture of the two substances with yellow mercuric oxide during an hour. The liquor is then decanted and distilled, when pure methylamine is obtained, providing no other nitrogenous bases are present in the impure liquor (François, J. Pharm. Chim. 1907, 25, 517, 523; Compt. rend. 1907, 144, 567; *ibid.* 1908, 147, 428).

To distinguish the three amines from ammonia the solution is neutralised with hydrochloric acid and evaporated to dryness. The residue is dissolved in 95 p.c. alcohol, and 5 c.c. of the solution is heated at 70°-75° with a few grammes of tetrachlorobenzoquinone. If any of the amines are present a violet coloration is produced, whereas ammonia gives no coloration (Tsalapatini, Chem. Zentr. 1908, i. 299). For the detection and estimation of ammonia in the methylamines, *see* François (Compt. rend. 1907, 144, 857). Methylamine can be distinguished from the di- and tri-amines by treatment with Nessler's reagent, with which it gives a yellow precipitate insoluble in excess of water and reagent. The other two amines form a white precipitate, which disappears on addition of water (Delépine, Compt. rend. 1896, 122, 1272).

Properties.—Methylamine is a colourless gas with a strong ammoniacal smell. It is very inflammable and burns with a yellow flame; it is decomposed at a red heat into ammonia, hydrocyanic acid, hydrogen, and marsh gas. It is very soluble in water, 1 volume of water at 12·5° dissolving 1150 volumes and 959 volumes at 25°. The solution behaves like *liquor ammoniæ* and yields crystallisable salts on neutralisation with acids.

Heat of neutralisation with hydrochloric acid =25·9 cals. (Muller, Ann. Chim. 1888, [vi.] 15, 517). For salts of methylamine, which, as a rule, resemble those of ammonia, *v.* Wurtz, *ibid.* [iii.] 30, 443; Topsoë, J. 1883, 618; Bailey, Chem. Soc. Trans. 45, 692; Petit and Polonowsky, Bull. Soc. chim. [iii.] 9, 1013; Brochet and Cambier, *ibid.* 13, 536; Jarry, Compt. rend. 1897, 124, 964; Cook, Amer. Chem. J. 1899, 22, 437; Ragland, *ibid.* 417; Lenher, J. Amer. Chem. Soc. 1898, 20, 572; Dunstan and Goulding, Chem. Soc. Trans. 1897, 579; Ladenburg, Ber. 1896, 29, 2711; Wende, *ibid.* 2719; Ristenpart, *ibid.* 2530; Partheil and Broich, *ibid.* 1897, 30, 618; Fenner and Tafel, *ibid.* 32, 3228; Delépine, Ann. Chim. [vii.] 8, 461; Compt. rend. 1896, 122, 1272; Hofmann and Marburg, Annalen, 1899, 305, 191; Lang, Chem. Soc. Trans. 1903, 724; Rengade, Compt. rend. 1905, 140, 246; François, *ibid.* 1906, 142, 1199; Litterscheid, Arch. Pharm. 1904, 242, 37; Guareschi, Chem. Zentr. 1891, ii. 620; Christensen, J. pr. Chem. [ii.] 45, 356; Gutbier and Woernle, Ber. 1906, 39, 4134.

Methylamine, like ammonia, in aqueous solution precipitates metallic hydroxides from solutions of many salts; but, unlike ammonia, dissolves, when in excess, the hydroxide of aluminium, whereas it fails to dissolve the hydroxides of cadmium, nickel, and cobalt.

When methylamine is oxidised with monopersulphuric acid (Caro's acid), according to Bamberger and Seligman, it undergoes the following changes:

$$CH_3NH_2 \rightarrow CH_3\cdot NH\cdot OH \rightarrow CH_2:NOH \rightarrow \text{either}$$
$$OH\cdot CH:NOH \text{ or } CH_2NH\cdot OH \rightarrow CH_3NO_2$$

hydrogen cyanide also being formed (Ber. 1902, 35, 4299). Unlike the di- and tri-amines, it is readily decomposed by chromic acid with evolution of nitrogen (Coninck and Combe, Compt. rend. 1898, 127, 1221; 128, 682).

Methylamine interacts with cyanogen chloride in cold ethereal solution forming principally *s*-dimethylguanidine hydrochloride and also methylcyanamide (Kaess and Gruszkiewicz, Ber. 1902, 35, 3598).

It also reacts slowly with sodium phosphate and magnesium sulphate in dilute aqueous solution, forming methylamine magnesium phosphate (François, J. Pharm. Chim. 1908, 28, 86). Neither di- nor tri-methylamines react thus.

Liquid methylamine is a very good solvent for organic compounds, and combines readily with both organic and inorganic compounds, forming addition products (Gibbs, J. Amer. Chem. Soc. 1906, 28, 1395; Hochstetter and Kohn, Monatsh. 1903, 24, 773). For a number of addition products with inorganic substances, *see* Bonnefoi, Compt. rend. 1897, 124, 773; 127, 516; Jarry, *l.c.*; and Ann. Chim. [vii.] 27, 376; Matthews, J. Amer. Chem. Soc. 1898, 20, 826; Lenher, *ibid.* 1900, 23, 486; Moissan, Compt. rend. 128, 26; Lang and Jolliffe, Chem. Soc. Proc. 1903, 147; Ephraim and Weinberg, Ber. 1909, 42, 4447; Ekeley, J. Amer. Chem. Soc. 1909, 31, 664.

In the presence of soil, calcium carbonate and oxygen, methylamine is converted into ammonia, and finally into nitrites and nitrates (Demoussy, Compt. rend. 1898, 126, 253).

Under the influence of the silent electric discharge methylamine evolves nitrogen (Berthelot, *ibid.* 775; *see also* Mixter, Amer. J. Sci. 1898, [iv.] 6, 217).

Methyl chloramine $Me\cdot NHCl$ is obtained by distilling methylamine hydrochloride with sodium hypochlorite (Berg. Compt. rend. 1893, 116, 887). It is a colourless volatile oil with a piquant irritating odour.

Methyl dichloramine $MeNCl_2$ is obtained by leading chlorine into aqueous methylamine (Kohler, Ber. 1878, 12, 771) or by the distillation of methylamine hydrochloride with bleaching powder (Bamberger and Renauld, Ber. 1895, 28, 1683). It is a golden-yellow liquid, b.p. 59°–60°. Similar bromo and iodo compounds are also known (Dehn, J. Amer. Chem. Soc. 1909, 31, 123).

Methyl nitramine MeN_2O_2H is obtained by treating δ-dimethyl dinitro-oxamide with barium hydroxide (Franchimont, Rec. trav. chim. 1894, 13, 313; 321, 331; also v. Pechmann, Ber. 1897, 30, 647). It forms long needles, m.p. 38°, readily soluble in water and in alcohol. On reduction with aluminium amalgam and aqueous alcohol it yields diazomethane, whilst with zinc and hydrochloric acid it is reduced to methylamine, hydrazine and methylhydrazine (Thiele and Meyer, Ber. 1896, 29, 962). When heated with *β*-naphthol, *β*-naphthol methyl ether is formed with evolution of nitrogen (Franchimont and Umbgrove, Rec. trav. chim. 1897, 15, 215). It forms a number of metallic salts (Franchimont, *l.c.*; Ley and Kissel, Ber. 1899, 32, 1364). The *potassium* salt $KMeO_2N_2$, m.p. 220°, explodes on heating or on being struck.

Thionylmethylamine $MeN:SO$ is an oil which fumes in air, b.p. 58°–59° (Michaelis and Storbeck, Annalen, 1893, 274, 187). Methylamine derivatives of various aliphatic acids are described by Duden, Bock and Reid (Ber. 1905, 38, 2036), Fosse (Compt. rend. 1906, 143, 914); Tafel and Wassmuth (Ber. 1907, 40, 2831); Benary (Ber. 1909, 42, 3912); Gansser (Zeitsch. physiol. Chem. 1909, 61, 16); Fourneau (Bull. Soc. chim. 1909, [iv.] 5, 229); also D. R. PP. 198306, 1908; 202167, 1909.

Methylaminoanthraquinones are prepared by dissolving a mixture of the desired amino-derivative of anthraquinone and formaldehyde in concentrated sulphuric acid and warming to 55°–60° (D. R. P. 156056, 1905).

α-**Methylaminoanthraquinone,** m.p. 167°, is obtained by treating α-mononitroanthraquinone with methylamine solution (D. R. P. 144634; Frdl. 1902–04, 201).

1-Methylaminoanthraquinone-5-sulphonic acid $SO_3H\cdot C_6H_3{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3NHMe$, and also the diamino compound

$$NHMe\cdot C_6H_3(CO)_2C_6H_3NHMe$$

are formed by treating potassium 1:5-anthraquinonedisulphonate with aqueous methylamine at 150°. The potassium salt of the former crystallises from water in violet-brown needles. Other methylamino anthraquinone sulphonic acids are obtained similarly (D. R. P. 186722, 1907).

For other derivatives of methylamine anthraquinone which are used as dyes, *see* D. R. PP. 156759, 164791; Frdl. 1905–07, 293, 280; D. R. PP. 212470, 1909; 220314; Chem. Zentr. 1901, i. 1306).

Methylaminoacetocatechol

$$C_6H_3(OH)_2CO\cdot CH_2\cdot NHMe$$

is formed by warming gently chloroacetocatechol with an excess of methylamine. It is a white crystalline powder darkening at 200° and decomposing at about 230°. Ferric chloride gives an emerald-green colour (D. R. P. 152814; Dakin, Chem. Soc. Proc. 1905, 154). When reduced and then treated with ammonia, it yields methylamino-*o*-dihydroxyphenylethanol, m.p. 208°, which is an astringent, and has hæmostatic properties (J. Soc. Chem. Ind. 1909, 1005). The ethanol yields a hydrochloride, m.p. 157° (D. R. P. 202169).

Methylaminoquinones are described by Fichter (Annalen, 1908, 361, 363).

2-Methylamino-8-methoxyquinoline crystallises in silver prisms, m.p. 151°, and forms a crystalline nitrosamine, m.p. 180° (Fischer, Ber. 1902, 35, 3674).

Methylaminocamphene has b.p. 202°–203°/756 mm. $[\alpha]_D + 28{\cdot}7°$ (Forster and Micklethwait, Chem. Soc. Trans 1904, 334).

Methylaminocoumarins are described by v. Pechmann and Schaal (Ber. 1899, 32, 3690, 3696); and by Morgan and Micklethwait (Chem. Soc. Trans. 1904, 1238).

Methylaminothiazoles are described by Young and Crookes (Chem. Soc. Trans. 1906, 68). *Uracils* by Wheeler and Jameson (Amer. Chem. J. 1904, 32, 342).

Dimethylamine $(CH_3)_2NH$; b.p. 7·2°–7·3° at 764·1 mm.; crit. temp. 164·6°, crit. press. 52·4 atm. (Berthoud); sp.gr. 0·6865 at - 5·8° (Hofmann, Ber. 1889, 22, 699). From methyl iodide and ammonia (Hofmann, J. 1862, 329). In small quantity by distilling the compound of aldehyde ammonia and sulphurous acid with caustic lime (Petersen, Annalen, 1857, 102, 317). In the putrefaction of fishes; occurs in herring brine (Bocklisch, Ber. 18, 87, 1924). Is obtained together with methylamine by the action of methyl alcohol on phospham (*see Methylamine*; also Vidal, Chem. Zentr. 1897, ii. 517).

Preparation.—The product of the action of ammonia upon methyl iodide (consisting of the hydriodides of mono-, di- and tri-methylamine and tetramethylammonium iodide) is treated with alcohol in order to remove the last-mentioned compound. The residue on treatment with caustic potash yields the free bases which can be partially separated by condensation, the more volatile monomethylamine escaping condensation may be received in hydrochloric acid.

The mixture of the free bases is then treated with ethyl oxalate, the trimethylamine remains unacted upon, the dimethylamine is converted into the ethyl ester of dimethyl oxamic acid, whilst the mono- base is converted into dimethyl oxamide. The latter is difficultly soluble in cold water, and is thus separated from the dimethylamine compound, which is then distilled with potash

$$(CH_3)_2N{\cdot}C_2O_2(OC_2H_5)+2KOH$$
$$=(KO)_2C_2O_2+C_2H_5OH+(CH_3)_2NH$$

The alcoholic solution is neutralised with hydrochloric acid, evaporated to dryness, and decomposed by caustic potash. The hydrochloride of dimethylamine can be freed from admixed ammonium chloride by treatment with chloroform, in which the latter is insoluble (Behrend, Annalen, 1883, 222, 119).

By the reduction of a mixture of formaldehyde and methylamine with zinc-dust and hydrochloric acid (D. R. P. 73812).

Dimethylamine can be obtained by heating thiodimethylamine (185 grammes) with sulphuric acid chlorhydrin (130 grammes), the temperature being raised gradually and the mass finally heated for 2–3 hours at 130°–150°. On cooling the product is shaken with ether to remove benzenethiochloride, and the residue is treated with water, made alkaline, and the dimethylamine is separated by distillation in steam (D. R. P. 105870; Frdl. 1897-1900, 34).

An almost theoretical yield of dimethylamine hydrochloride is obtained by adding powdered nitrosodimethylaniline hydrochloride and a few zinc shavings to a nearly boiling, dilute aqueous solution of sodium hydroxide, the amine being absorbed in concentrated hydrochloric acid contained in a Péligot's U-tube (Menschutkin, J. Russ. Phys. Chem. Soc. 1898, 30, 243; Norris and Laws, Amer. Chem. J. 1898, 20, 54).

The free base can be liberated by treatment with caustic soda.

Properties.—Dimethylamine is a colourless, inflammable liquid with a strong ammoniacal smell. Bromine acts upon an aqueous solution forming dimethylamine hypobromite and bromide $N(CH_3)_2H{\cdot}HBrO$ and $NH(CH_3)_2{\cdot}HBr$; or, if the bromine be in excess, the unstable tribromide $N(CH_3)_2Br_3$, a yellow flocculent precipitate, is obtained (Raschig, Ber. 1885, 18, 2250).

At 0° it combines directly with two atoms of bromine (Remsen and Norris, Amer. Chem. J. 18, 94).

When oxidised with hydrogen peroxide it yields nitrous acid, formaldehyde and formic acid (Dunstan and Goulding, Chem. Soc. Trans. 1899, 1009). With Nessler's reagent, dimethylamine gives a white precipitate.

When heated with hydrogen at 820°–1120°, hydrocyanic acid, methane and ammonia are formed, the relative quantities of the products depending on the quantity of hydrogen present (Voerkelius, Chem. Zeit. 1909, 33, 1025, 1078, 1090).

Dimethylamine forms salts resembling those of ammonia (Topsoe, J. 1883, 618; Delépine, Ann. Chim. [vii] 8, 459; Norris and Laws, *l.c.*; and 490; Ragland, *l.c.*; Cook, *l.c.*; Jorgensen, Zeitsch. anorg. Chem. 1906, 48, 374).

Dimethylamine dihydrochloride is a white crystalline substance formed by passing dry hydrogen chloride into the base or into the normal hydrochloride (Kaufler and Kunz, Ber. 1909, 42, 385).

Dimethylchloramine Me_2NCl, b.p. 46°/765 mm., is obtained in the same way as the monomethyl derivative, and has similar properties (Berg. *l.c.*). The corresponding bromo derivative has b.p. 64°–66° (Schwanoff, Ber. 1893, 26, 423; Willstatter and Hottenroth, Ber. 1904, 37, 1775).

Other halogen derivatives are described by Cohn (J. pr. Chem. 1897, [ii.] 56, 345) and Knorr (Ber. 1904, 37, 3504).

Dithiodimethylamine $S_2(NMe_2)_2$ is a reddish-yellow liquid, b.p. 82°–83°/22 mm., 170°–180°/760 mm. (decomp.). It is decomposed by acids into the amine, sulphur, and sulphur dioxide (Michaelis and Luxembourg, Ber. 1895, 28, 165).

Dimethylnitramine $Me_2O_2N_2$ forms bright colourless needles, whilst the *isonitramine* is a liquid, b.p. 112° (Franchimont and Umbgrove, *l.c.*; Lachman, Amer. Chem. J. 1899, 21, 483; Bamberger, Ber. 1895, 28, 402; Kirpal, *ibid.* 537).

Dimethylamine acetone $NMe_2{\cdot}CH_2{\cdot}COMe$ is prepared by adding chloracetone to an aqueous 30 p.c. solution of dimethylamine. It is a colourless oil, b.p. 123°, miscible with water, yielding a platinochloride, which forms beautiful crystals, m.p. 176° (decomp.). It also yields a hydrochloride; an aurichloride (m.p. 145°–146°); a methiodide (m.p. 168°); and an oxime, m.p. 99° (Stoermer and Dzimski, Ber. 1895, 28, 2220; 1896, 29, 866).

Methyl dimethylaminoacetate is a volatile oil, boiling at 135°. The corresponding ethyl compound boils at 149°–150°.

Methyl β-dimethylaminopropionate

$$NM_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me$$

b.p. 154·5°, yields a methiodide, m.p. 191°–192° (decomp.), which, when warmed with alkalis, gives acrylic acid and trimethylamine, whilst with silver oxide it gives β-trimethylpropiobetaine (Willstatter, Ber. 1902, 35, 584).

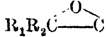
Methyl-γ-dimethylaminobutyrate has b.p. 171·5°–173°, and yields a crystalline aurichloride and picrate.

Dimethylaminodimethylacetal is a colourless mobile liquid, b.p. 137·5°, which has no reducing properties. Other dimethylamino derivatives of aliphatic acids have also been prepared (Willstätter, Ber. 1902, 35, 1378).

Dimethylamino derivatives of aliphatic hydrocarbons are described by Willstatter (Ber. 1901, 34, 129; Annalen, 1903, 326, 1); Duden and Lemme (Ber. 1902, 35. 1335); Hochstetter and Kohn (Monatsh. 1903, 24, 773); Bouveault (Bull. Soc. chim. 1904, [iii.] 31, 1306, 1322).

A number of methyl and dimethyl aminocarbinol derivatives of the type

$$R_1R_2C(OH)CH_2NR_3R_4$$

(where R_1, R_2=alkyl or aryl groups, R_3= methyl or other alkyl, and R_4=an alkyl group or hydrogen) are obtained by the action of methyl or dimethylamine on an ethylene oxide  $R_1R_2\overset{O}{C{-}{-}{-}CH_2}$ (D. R. P. 199148; Frdl. 1908–10, 975; also D. R. P. 173610; Knorr and Matthes, Ber. 1901, 34, 3482).

These substances, which have valuable anæsthetic properties, and are less toxic than cocaine or eucaine, can also be obtained by treating aminoacetones or esters of amino acids containing a tertiary amino group with magnesium organo compounds of the type R·Mg·X (D. R. PP. 169819, 169746; Frdl. 1905–07, 1029, 1033).

Esters having pronounced soporific properties and a low toxicity are produced by condensing alkyl dimethylaminohydroxy*iso*butyrates with anhydrous chloral (D. R. PP. 203643, 198306, 202167; Frdl. 1908–10, 980, 984, 1000).

For other dimethylamino compounds used in medicine, *see* D. R. PP. 121051, 129967; Frdl. 1900–02, 1219, 1226; J. Soc. Chem. Ind. 1909, 491.

Dimethylaminoparaxanthine known in commerce as *paraxine*, is an energetic diuretic (D. R. P. 156901, 1905) and is decomposed into **2 : 6-Dioxy-8-dimethylamino-7-methylpurine,** m.p. above 319°, a crystalline substance which can be separated from the urine and has also a strong diuretic action (Forschbach and Weber, Arch. exp. Path. Pharm. 1907, 56, 186).

Dimethylamine reacts in equimolecular proportion with polyhydroxyaromatic compounds forming addition products with an alkaline reaction which can be used for developing in photography without further addition of alkali (D. R. P. 141101; Frdl. 1900–02, 1217).

Dimethylamine is used in the production of a large number of valuable dyestuffs; thus violet to blue dyestuffs are obtained by heating gallocyanine with mono- di- or tri-methylamine (D. R. PP. 57459, 65000; Frdl. 1890–94, 367).

Blue dyes are also obtained by the action of dimethylamine on the dyes of the oxazine series. The substances so obtained differ from the parent dye in giving purer colours and in being stable towards alkalis (D. R. P. 54658; Frdl. 1890–94, 373).

See also Freund and Wirsing, Ber. 1907, 40, 204; D. R. PP. 172079, 161665; the article on AMINES and the various parent dyes.

When dimethylamine is heated with *p*-aminophenol-azo-β-naphthol and formaldehyde, a dark-brown powder is obtained, which is a good dye for tanned cotton (D. R. P. 95546; Frdl. 1897–1900, 555).

3-Dimethylaminoanthraquinone is obtained when dimethylaminobenzoylbenzoic acid (1 part) is heated with concentrated sulphuric acid (10 parts) at 175°–180°. It forms red needles, m.p. 181°. When 12 parts of sulphuric acid is used, and the temperature is kept at 80°, dimethyl-aminoanthranol is formed, but is readily oxidised to the anthraquinol by ferric chloride (Haller and Guyot, Compt. rend. 1898, 126, 1544; D. R. P. 108837).

1-Dimethylamino-5-phenoxyanthraquinone, m.p. 147°–149°, and similar compounds which form important materials for the manufacture of dye-stuffs, have been obtained by treating the corresponding anthraquinone derivative with the desired mono- or di-alkylamine in pyridine solution at 110°–115° (D. R. P. 165728; Frdl. 1905–7, 289).

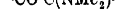
For other dimethylaminoanthraquinone derivatives, *see* Severin, Compt. rend. 1906, 142, 1274; D. R. PP. 136777, 136778; Frdl. 1900–02, 374; D. R. P. 146691; Frdl. 1902–04; D. R. PP. 146691, 1904; 205096, 1909).

Dimethylamine, when heated with fluorescein chloride or dichlorofluorescein chloride in presence of zinc chloride at 160°–170°, gives derivatives of chloroaminofluoran, whilst at higher temperatures rhodamines are produced (D. R. P. 139727, 1903).

Chloromethyl- and dimethyl-aminofluoran form pink crystals, melting at 168° and 218° respectively.

Dimethylaminocamphor is a colourless oil, b.p. 241°/758 mm. It does not reduce Barreswil's solution, and is only slowly acted on by silver nitrate. It forms a picrate, m.p. 220° (decomp.); hydriodide, m.p. 251° (decomp.); a platinichloride, m.p. 211° (decomp.); and acetate, m.p. 251°, with evolution of gas (Forster, Chem. Soc. Trans. 1905, 240; Rabe and Schneider, Ber. 1908, 41, 872).

5-Dimethylaminouracil



$$NH\begin{matrix}\diagup CO{-}{-}{-}NH \diagdown \\ \diagdown CO{\cdot}C(NMe_2) \diagup\end{matrix}CH$$

is formed by treating 5-bromouracil with dimethylamine, and forms colourless plates, m.p. 297° (decomp.) (Wheeler and Jamieson, Amer. Chem. J. 1904, 32, 342).

Trimethylamine $N(CH_3)_3$; b.p. 3·2°–3·8° at 764·6 mm., sp.gr. 0·662 at −5·2° (Hofmann, Ber. 22, 699; sp.gr. 0·673 at 0° (Bleunard). Does not solidify at −75° under a pressure of 10 mm.; forms a crystalline hydrate with 7 molecules of water, melting at 4·3°. Occurs in certain plants, *e.g. Chenopodium Vulvaria* (Linn.), *Arnica montana* (Linn.), *Rhagodia hastata* (Australian Salt Bush), hawthorn blossom, pear and wild cherry blossom, in ergot (Dessaignes, J. 1857, 481; Walz, J. 1852, 552), in certain lichens such as the *Sticta fuliginosa*, in hops and in cod-liver oil, in bone oil and guano (Zopf, Annalen. 1897, 297, 272). It also occurs in various animal fluids, *e.g.* in calves' blood (Dessaignes), and in human urine (Filippi, Zeitsch. physiol. Chem. 1906, 49, 433). Also in large quantities in herring brine, which owes to it its peculiar smell (Wertheim, J. 1851, 480).

It is also a product of the decomposition of fibrin by *streptococci* (Emmerling, Ber. 30, 1863).

It is obtained by treating methyl iodide with ammonia (Hofmann); by the distillation of tetramethylammonium hydroxide (Hofmann, Annalen, 93, 325); by distillation of narcotine (Wertheim, *ibid.* 73, 208), or codeine (Anderson, *ibid*, 77, 367), with potash.

By the action of methyl alcohol on magnesium nitride (Szarvasy, Ber. 1897, 30, 305). By the reduction of trimethyloxamine with zinc-dust (Hantzsch and Hilland. Ber. 1898, 31, 2058; Dunstan and Goulding, *l.c.*). By the interaction of hexamethylenetetramine with formaldehyde (Eschweiler, Ber. 1905, 38, 880).

By heating a mixture of ammonium chloride (1 part) and trioxymethylene (2·65 parts) under reflux at 120°–170° (Schmitz, D. R. P. 270260).

By heating a mixture of ammonium chloride and formaldehyde (*cf.* Methylamine). *Cf.* Werner, Chem. Soc. Trans. 1917, 111, 844.

By the putrefaction of yeast or of wheat meal (Hesse, J. 1857, 403). Also by the dry distillation of 'vinasses' from the beetroot sugar manufacture (Vincent, Bull. Soc. chim. [ii.] 27, 150).

Preparation.—The crude methylamine from the distillation of the 'vinasse' is treated with sulphuric acid, the solution evaporated to a syrup and treated with absolute alcohol, the monomethylamine sulphate is thus precipitated. The filtrate is treated with the proper amount—1 molecule for every 2 molecules of primary amine present—of ethyl oxalate, and allowed to stand for 24 hours. The precipitate, consisting of a mixture of di-*iso*butyl oxamide and di-*iso*propyl oxamide, is filtered off and the filtrate distilled; the residue is then decomposed by potash, the free bases received in alcohol, and the alcoholic solution mixed at 0° with ethyl oxalate (1 molecule to each molecule of free base) and allowed to stand for a day. The mixture is then distilled, and the triethylamine obtained pure. The non-volatile residue is made slightly alkaline with milk of lime and evaporated, calcium *iso*propyl oxamate first crystallises out, and then calcium ethyl oxamate. The mother liquor, on addition of alcohol, gives a precipitate of calcium methyl oxamate, whilst calcium dimethyl oxamate remains in solution (Duvillier and Buisine, Ann. Chim. [v.] 23, 299).

A mixture of herring pickle and lime is subjected to distillation, the alkaline distillate is neutralised with hydrochloric acid, evaporated to dryness, and the residue treated with alcohol, which leaves the ammonium chloride undissolved. The solution is evaporated, the residue dissolved in a little water, and redistilled with lime, the vapours being led through an empty bottle to separate less volatile constituents, and then conducted into water or condensed with ice.

50 grammes of ammonium chloride are heated with 440 grams of 40 p.c. formaldehyde solution in an autoclave at 120°–160°.

Trimethylamine can more readily be obtained in a pure state by the distillation of tetramethylammonium hydroxide (Schmidt, Annalen, 1892, 267, 254).

Properties.—Trimethylamine is a volatile liquid with a strong, fish-like smell. It is very soluble in water, and possesses strong basic properties, although it can be displaced from its compounds by either mono- or di-methylamine. It is not acted upon by formaldehyde, and hence it may be determined in presence of ammonia (Budai, Zeitsch. physiol. Chem. 1913, 86, 107).

When heated at 800°–1000° it decomposes almost quantitatively into hydrocyanic acid and methane, whilst at 600°, *tetramethyl hydrazine* is formed (Voerkelius, Chem. Zeit. 1909).

When passed through a hot tube with hydrogen it decomposes, forming dimethyl dimethylene diamine $(CH_2)_2(CH_3)_2N_2$, ammonia, cyanogen, and other products (Romeny, Ber. 11, 835). It forms salts with acids, of which the hydrochloride is of some importance; it has been suggested to employ it in the manufacture of potassium carbonate from potassium chloride by a process analogous to the Solvay ammonia soda process. Ammonia cannot be employed in this process, since ammonium chloride has only about the same solubility as potassium hydrogen carbonate, whilst trimethylamine hydrochloride is very much more soluble.

For a number of salts formed by trimethylamine with inorganic salts, *see* Guareschi, *l.c.*; Christensen, *l.c.*; Ragland, *l.c.*; Cook, *l.c.*; Hofmann and Marburg, *l.c.*; Mylius and Foerster, Ber. 24, 2424; Wiede, *ibid.* 31, 3140; Michael and Hibbert, Annalen, 1909, 364, 64.

Trimethylamine dibromide NMe_3Br_2 is formed by passing dry trimethylamine into ice-cold bromine, or by heating trimethylamine hydrobromide (1 molecule) with a small quantity of hydrogen bromide and bromine (1 molecule). Similar iodine, chlorine, and mixed halogen derivatives have also been obtained (Remsen and Norris, Amer. Chem. J. 1896, 18, 90; *see* also Hantzsch and Graf, Ber. 1905, 38, 2154; Norris, *ibid.* 3904). They are crystalline unstable substances.

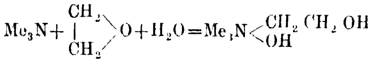
For other halogen and halogen acid compounds of trimethylamine, *see* Gabriel and Stelzner, Ber. 1895, 28, 2929; Delépine, Compt. rend. 1896, 122, 272; Ann. Chim. 1896, [vii.] 8, 439; Norris, Amer. Chem. J. 1898, 20, 51; Pictet and Krafft, Bull. Soc. chim. [iii.] 7, 72; Hantzsch, Ber. 1905, 38, 2161; Kaufler and Kunz, *ibid.* 1909, 42, 2482).

Trimethylamine combines with carbon disulphide to form a colourless crystalline compound

$N(CH_3)_3CS_2$, m.p. 125°, which is somewhat unstable; it is soluble in chloroform, and combines with dilute acids, but is decomposed by strong acids into its constituents.

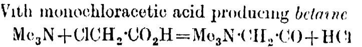
Trimethyloxamine (*Trimethylamine oxide*) $Me_3N:O,2H_2O$ forms needle-shaped crystals, m.p. 96°, and is best obtained by the action of hydrogen peroxide on an aqueous solution of trimethylamine (Dunstan and Goulding, Chem. Soc. Trans. 1899, 794, 1005; Mamlock and Wolffenstein, Ber. 1901, 34, 2499).

Trimethylamine, like dimethylamine, enters into the constitution of a number of important dyes. It also yields derivatives which form substances important physiologically; thus it reacts with ethylene oxide forming *choline*



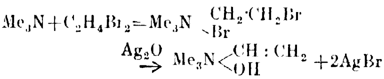
$$Me_3N+\left|\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle O+H_2O=Me_3N\langle\begin{matrix}CH_2\cdot CH_2\cdot OH\\OH\end{matrix}$$

With monochloracetic acid producing *betaine*



$$Me_3N+ClCH_2\cdot CO_2H=\underbrace{Me_3N\cdot CH_2\cdot CO}_{O}+HCl$$

With ethylene dibromide, to form *neurine*



$$Me_3N+C_2H_4Br_2=Me_3N\langle\begin{matrix}CH_2\cdot CH_2Br\\Br\end{matrix}\xrightarrow{Ag_2O}Me_3N\langle\begin{matrix}CH:CH_2\\OH\end{matrix}+2AgBr$$

*iso*Crotyltrimethylammonium bromide

$CMe_2:CH\cdot NMe_3Br$

obtained by the interaction of *iso*butylene bromide and trimethylamine, is homologous with neurine bromide, and, like valeryltrimethyl ammonium bromide, closely resembles it in its physiological action. Dibrom*iso*butyl trimethyl ammonium bromide and dibrom*iso*butyltrimethyl ammonium dibromide and other similar compounds have also been prepared (Kleine, Chem. Zentr. 1894, i. 16).

Ethylene bromide reacts with trimethylamine in molecular proportion at 100°, yielding tetramethylammonium bromide, trimethylvinylammonium bromide (neurine bromide), dimethylamine bromide, and other compounds.

Propylene and amylene bromides also react with trimethylamine yielding a number of methylammonium compounds (Kleine, *l.c.*).

Trimethylamine reacts with halogen ketones, forming ketonic bases (Schmidt, Arch. Pharm. 1898, 236, 334).

Trimethylacetonylammonium chloride (*coprine chloride*) $AcCH_2\cdot NMe_3Cl$ is a crystalline substance which gives a platinochloride, yellowish red needles, m.p. 238°–240°; an aurichloride, beautiful yellow needles, m.p. 139·5°; and an oxime, colourless plates, m.p. 212° (Furnée, Arch. Pharm. 1898, 236, 334).

Trimethylacetonylammonium bromide melts at 190°, and at 195° it gives rise to a yellow distillate, and tetramethylammonium bromide (Brendler and Tafel, Ber. 1898, 31, 2683).

For the interaction of trimethylamine with other aliphatic compounds, *see* Malbot, Bull. Soc. chim. [iii.] 6, 845, 709, 711; *ibid.* 7, 213; Duvillier, *ibid.* [iii.] 23, 507; Menozzi and Pantoli, Gazz. chim. ital. 23, ii. 209; Hartmann, Chem. Zentr. 1896, i. 999; André, Compt. rend. 1998, 126, 1107; Benary, Ber. 1908, 41, 2399; D. R. P. 195813; Frdl. 1908-10, 990.

In France and in Russia trimethylamine has been employed successfully in medicine, but English and American doctors have not obtained such good results. For the physiological effects of trimethylamine, *see* Combemale and Brunelle, Compt. rend. Soc. Biol. 1891, 175.

Methylammonium cobaltinitrite

$(MeNH_3)_3CO(NO_2)_6$

is prepared by adding to a nearly saturated solution of methylamine hydrochloride, a nearly saturated solution of pure sodium cobaltinitrite. It is a yellow powder, stable when dry, but slowly decomposing in the presence of moisture or on heating. When treated with strong mineral acids it decomposes violently (Cunningham and Perkin, Chem. Soc. Trans. 1909, 1564).

Monomethylammonium hexabromoplatinate $(NH_3Me)_2PtBr_6$ and the corresponding di- and tri-methyl compounds are all crystalline substances (Gutbier and Bauriedel, Ber. 1909, 42, 4243).

Magnesium methylammonium arsenate

$NH_3Me\cdot MgAsO_4,8H_2O$

and the trimethylammonium compound

$NHMe_3\cdot MgAsO_4,6H_2O$

are white crystalline powders (Brisac, Bull. Soc. chim. 1903, [iii.] 29, 591). Similar methylammonium phosphates have also been prepared (Poicher and Brisac, *ibid.* 587). For other methyl ammonium compounds, *see* Reynolds, Chem. Soc. Trans. 1891, 394; François, Compt. rend. 1905, 140, 1697; Gutbier, Zeitsch. physikal. Chem. 1909, 69, 304.

Tetramethylammonium $N(CH_3)_4$, *tetramethylium*, according to Palmaer (Zeitsch. Elektrochem. 1902, 8, 729) is produced when a solution of tetramethylammonium chloride or hydroxide in liquid ammonia is electrolysed between platinum electrodes, but it could only be observed as giving a transient blue coloration and could not be isolated.

The base, **Tetramethylammonium hydroxide** NMe_4OH is formed as the pentahydrate

$NMe_4OH,5H_2O$

m.p. 62°–63°, by the action of a methyl alcohol solution of potassium hydroxide on a similar solution of tetramethyl ammonium chloride. When this hydrate is desiccated it forms a trihydrate, m.p. 59°–60°, and a monohydrate which decomposes at 130°–135° without melting (Walker and Johnson, Chem. Soc. Trans. 1905, 955). The hydroxides are hygroscopic, strongly alkaline, and readily absorb carbon dioxide when exposed to the air. When heated they decompose forming methyl alcohol and trimethylamine. The *iodide* $N(CH_3)_4I$ is the main product of the action of ammonia upon methyl iodide (Hofmann, Proc. Roy. Soc. 1851, 381), or by heating trimethylazonium iodide with methyl iodide at 125°–130° (Harries and Haga, Ber. 31, 59). It forms quadratic prisms soluble in hot water, but only slightly in cold water; sp.gr. 1·84 (Schröder, Ber. 12, 562). Similar chlorine and bromine compounds are also known.

Tetramethylammonium pentaiodide NMe_4I_5, m.p. 126°–127°, is obtained by the action of methyl iodide on nitrogen iodide (Silberrad and Smart, Chem. Soc. Trans. 1906, 173).

Tetramethylammonium forms many salts which have the power of producing crystalline double compounds with many metallic salts (*v.* Topsöe, J. 1883, 619; Risse, Annalen, 107, 223;

Lossen, *ibid.* 181, 374; Ragland, *l.c.*; Prescott, J. Amer. Chem. Soc. 1898, 20, 96; Wiede, *l.c.*; Auld and Hantzsch, Ber. 1905, 38, 2685; Milbauer, Zeitsch. anorg. Chem. 1907, 53, 135; Schmidt, Chem. Zentr. 1907, ii. 1593; Braun, Ber. 1908, 41, 2128; Kaufler and Kunz, *l.c.*).

Tetramethylammonium formate (*Forgenine*) $H\cdot CO_2\cdot N(CH_3)_4$ is obtained by the action of tetramethylammonium iodide on silver formate. It is a white crystalline, odourless, hygroscopic substance, stable in dry air and in solution, decomposing above 200°, and giving the reactions of formates (Vanzetti, Chem. Zentr. 1906, ii. 1347).

Forgenine is employed in medicine, but in large doses it is toxic, and may even prove fatal (Piccinini, Chem. Zentr. 1907, i. 651).

α-**Methyl hydroxylamine** $MeO\cdot NH_2$ is formed by treating methyl ethyl benzhydroxamate with hydrochloric acid (Lossen and Zanni, Annalen, 1876, 182, 225). The hydrochloride forms prisms, m.p. 149°, and gives an orange-red crystalline platinochloride (Lossen, Ber. 1883, 16, 827; Petraczek, *ibid.* 827).

β-**Methyl hydroxylamine** MeNH·OH is formed by heating benz*syn*aldoxime methyl ether or its nitro derivative with hydrochloric acid (Dittrich, Ber. 1890, 23, 3598; Kjellin, *ibid.* 1893, 26, 2382), but is best prepared by the electrolytic reduction of nitromethane in alcoholic sulphuric acid solution at 15°–20° (Pierron, Bull. Soc. chim. [iii.] 21, 783; *see* also Bamberger, Ber. 1894, 27, 1350; Kirpal, *ibid.* 1882, 25, 1715). It forms long prisms, m.p. 42°, b.p. 62·5°/15 mm., sp.gr. 1·0003 at 20°/4°. It is readily soluble in water and alcohol, decomposes on standing, and is reduced to methylamine by hydriodic acid.

The *hydrochloride* has m.p. 88° 90°; the *picrate* m.p. 128°–130°.

α-**Methyl** *β*-**ethyl hydroxylamine** NHEtOMe is a colourless alkaline liquid, b.p. 60°–61°, readily soluble in water and does not reduce silver nitrate. It forms a hydrochloride and a platinichloride. *β-Methyl α-ethyl hydroxylamine* has b.p. 65°–65·5° and similar properties to the *α*-methyl *β*-ethyl compound (Jones, Amer. Chem. J. 1907, 38, 253).

αβ-**Dimethylhydroxylamine hydrochloride**

NHMe·OMe,HCl

forms long prismatic needles m.p. 115°–116°. It is volatile at 100°, does not reduce Barreswil's solution or silver nitrate. The platinochloride forms red prismatic crystals which melt at 180° (decomp.). The free base is a colourless volatile liquid, b.p. 42·2°–42·6° (Jones, Amer. Chem. J. 1898, 20, 1).

Methyl hydrazine $CH_3HN\cdot NH_2$ is prepared by the reduction of diazomethane with sodium amalgam and alcohol, or by agitating methyl iodide with excess of methylhydrazine in aqueous solution (Pechmann, Ber. 1895, 28, 859; Harries and Haga, *ibid.* 1898, 31, 56). A colourless liquid with ammoniacal smell. The sulphate $NHCH_3\cdot NH_2,H_2SO_4$, a crystalline compound, is obtained from methyl hydrazine carbamide which results from the action of nascent hydrogen upon nitroso-methyl carbamide $NH_2\cdot CO\cdot N(CH_3)NO$ (Brüning, Ber. 21, 1899). The oxalate has m.p. 166°. Methyl hydrazine gives benzoyl and other derivatives (Michaelis and Hadanck, Ber. 1908, 41, 3285).

as-**Dimethyl hydrazine** $(CH_3)_2N\cdot NH_2$; b.p. 62·5° at 717 mm.; sp.gr. 0·801 at 2·2°; b.p. 63·9° at 752·5 mm.; sp.gr. 0·7914 at 22·3°/0° (Brühl, Ber. 1897, 30, 160); from nitroso-dimethylamine and nascent hydrogen (zinc-dust and acetic acid) in alcoholic solution (Renouf, Ber. 1880, 13, 2171), or by the dry distillation of trimethylazonium hydroxide (Harries and Haga, *l.c.* 58). It has a strong ammoniacal smell, and is very soluble in water, alcohol, or ether. It is decomposed by nitrous acid into nitrous oxide and dimethylamine.

The *oxalate* has m.p. 142°–143°. The *cyanide* crystallises in beautiful needles and decomposes at 0°–10° (Peters, Ber. 1906, 39, 2784).

sym-**Dimethyl hydrazine** MeNH·NHMe is obtained by the action of methyl iodide on potassium or lead diformyl hydrazine (Harries and Klamt, Ber. 1895, 28, 504; Harries and Haga, *l.c.* 63), or by boiling the methyl iodide salt of methyl pyrazole with strong potassium hydroxide (Knorr and Köhler, Ber. 1906, 39, 3257; Knorr, *ibid.* 3265). It is a mobile, colourless, fuming liquid, b.p. 81°/747 mm., with the characteristic odour of aliphatic hydrazines. It dissolves in water with evolution of heat, attacks cork, rubber, and the epidermis, and its vapour, when mixed with air, burns with a faintly luminous flame, depositing soot, and is liable to explosion It is a fairly strong reducing agent, and forms salts with mineral and organic acids. It also forms a semicarbazide and a phenylthiosemicarbazide, m.p. 115°; a dibenzoyl derivative, m.p. 85°; a dimethyl picrazide, m.p. 141°, and other derivatives (Knorr and Kohler, *l.c.*).

Trimethylazonium iodide $NH_2\cdot NMe_3I$ is obtained by agitating an aqueous solution of hydrazine hydrate with methyl iodide and caustic potash. It resembles ammonium chloride in crystalline structure, and has m.p. 235° (decomp.). It is converted into hydrochloride when acted on by silver chloride, and into the hydroxide by its interaction with silver oxide (Harries and Haga, *l.c.*).

Tetramethyl tetrazone $(CH_3)_2N\cdot N{:}N\cdot N(CH_3)_2$, b.p. 130°; a yellow explosive oil, slightly soluble in water. It is a strong base, and its salts are very soluble in water; it reduces silver solution with formation of a mirror (Renouf).

Methylene Compounds.

Methylene CH_2, a dibasic radicle not known in the free state.

Methylene diacetate $CH_2(C_2H_3O_2)_2$. B.p. 170°; from methylene iodide and silver acetate (Butlerow, Annalen, 107, 111); from chlormethyl acetate $C_2H_3O_2\cdot CH_2Cl$ and potassium acetate (Henry, Ber. 1873, 739). A liquid decomposed by water at 100° into acetic acid and trioxymethylene.

Methylene bromide CH_2Br_2, *Dibromomethane*. B.p. 96·5°–97·5° corr.; sp.gr. 2·4985 at 15°/15°, 2·47745 at 25°/25° (Perkin, Chem. Soc. Trans. 1884, 520). Obtained by the action of bromine upon methylene iodide under water (Butlerow, Annalen, 111, 251); from methyl bromide and bromine at 250° (Steiner), or by the action aluminium bromide heated to 100° on trioxymethylene (Gustavson).

A liquid which, by the action of water and excess of lead oxide at 150° gives ethylene glycol (Eltekoff, Ber. 6, 558).

Methylene chloride CH_2Cl_2, *Dichlormethane.* B.p. 41·6° corr.; sp.gr. 1·37777 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 195); b.p. 40°; sp.gr. 1·33771 at 15°/15°, 1·32197 at 25°/25° (Perkin, *ibid.* 1884, 527); b.p. 40·41° (corr.) (Thorpe and Rodger). From methane and chlorine after preliminary formation of methyl chloride (Regnault, Annalen, 33, 328); from methylene iodide and chlorine (Butlerow, Annalen, 111, 251).

Preparation.—A mixture of chloroform (1 vol.), zinc, and alcohol (3 vols.) is gradually treated with hydrochloric acid and distilled; the distillate, consisting of chloroform and methylene chloride, is rectified, and the residue boiling above 53° is again treated with zinc (Greene, Chem. News, 50, 75). It may also be prepared by treating methylene iodide under water with chlorine.

Properties.—A colourless liquid with a pleasant smell, resembling that of chloroform. When heated with water to 200°, hydrochloric and formic acids and methyl chloride are produced; the latter, on further heating, forming methyl alcohol and hydrochloric acid. With aqueous ammonia at 140° it forms ammonium chloride, methylamine hydrochloride, and formic acid (André, Compt. rend. 102, 1474). When treated with ammonia, dissolved in methyl alcohol, hexamethylenetetramine is obtained.

Methylene chlorobromide CH_2ClBr, *Chlorobromomethane.* B.p. 68°–69° at 765 mm.; sp.gr. 1·9907 at 19°/19°; V.D.=4·43 (Henry, Compt. rend. 101, 599). Obtained by the action of bromine upon chloriodomethane. A mobile colourless liquid, with agreeable smell. It gives rise when treated with 2 mols. of ammonia in saturated methyl alcohol solution for 2 hours at 60°–70° to hexamethylenetetramine hydrobromide, ammonium chloride, and ammonium bromide.

Methylene chlorofluoride CH_2ClF, *Chlorfluormethane.* A gas, V.D. 34·18 (calc. 34·25). From methyl fluoride and chlorine in sunlight. Is colourless, and slightly soluble in, and slowly decomposed by, water; burns with difficulty in oxygen (Collie, Chem. Soc. Trans. 1889, 412).

Methylene chloroiodide CH_2ClI, *Chloriodomethane.* B.p. 109°–109·5° at 760·4 mm.; sp.gr. 2·444 at 14·5°/14·5°; V.D. 88·14. An oily liquid obtained by the action of iodine monochloride upon methylene iodide (Sakurai, Chem. Soc. Trans. 1885, 198); also by action of iodine in potassium iodide solution upon monomercuric methylene chloriodide (*ibid.* 1882, 362).

Methylene iodide CH_2I_2, *Diiodomethane.* M.p 4°; b.p. 180°, with partial decomposition; sp.gr. 3·3326 at 15°/15° (Perkin, Chem. Soc. Trans. 1896, 1173); M.M. at 15°=18·827 (Perkin, *ibid.* 45, 464). From iodoform and sodium ethoxide (Butlerow, Ann. Chim. [iii.] 53, 313); by heating iodoform either alone or with iodine (Hofmann, Annalen, 115, 267; Dunn, Chem. Soc. Proc. 1910, 116); from chloroform or iodoform and hydriodic acid (Lebon, Zeitsch. Chem. 1868, 712). By the action of iodine on diazomethane dissolved in ether (*v.* Pechmann, Ber. 1894, 1889). A yellow liquid which, when heated with water and copper to 100°, yields ethylene (Butlerow, Annalen, 120, 356). With zinc ethyl it forms butane. With silver acetate yields methylene acetate; combines with mercury to form mercuric methylene iodide CH_2I,HgI. It dissolves phosphorus very readily at ordinary temperatures (more than 1 : 1). An attempt to prepare the radicle methylene (CH_2), by heating with silver powder produces carbon, methane and ethane and other products (Sudborough, Chem. Zentr. 1897, ii. 180). Methylene iodide, on account of its high density, is employed in the mixed solutions used for determining the sp.gr. of rocks and minerals by flotation, the usual diluents being benzene or ether.

Methylene oxide CH_2O *v.* FORMALDEHYDE.

Methylene sulphides.

Trimethylene sulphide $(CH_2S)_3$, *Parathioformaldehyde.* B.p. 216°; sublimes without decomposition. Formed by the action of sulphuretted hydrogen upon a solution of formaldehyde. Also by reducing, by means of zinc and hydrochloric acid, carbon disulphide (Girard, Annalen, 100, 306), potassium thiocyanate, or allyl mustard oil (Hofmann, Ber. 1, 176). It also results from the action of potassium sulphide on methylene iodide (Husemann, Annalen, 126, 294; Mansfeld, Ber. 1886, 698). It crystallises from benzene, carbon disulphide, or chloroform in quadratic prisms which are insoluble in water and possess a penetrating odour. It forms crystalline compounds with many salts, *e.g.* $C_3H_6S_3.HgCl_2$, needles, insoluble in water; $2C_3H_6S_3{\cdot}PtCl_4$, golden-yellow needles.

Metathioformaldehyde $(CH_2S)x$ is formed by leading sulphuretted hydrogen for 10 hours into a boiling solution of hexamethylenetetramine saturated with ammonia (Wohl, Ber. 1886, 2345). The precipitate is purified by washing with water and hydrochloric acid, and by boiling with alcohol and glacial acetic acid. It has a characteristic odour, melts at 175°–176°, is not volatile without decomposition, and does not form salts with mercuric or platinic chlorides.

Methylene hydrogen sulphide $CH_2(HS)_2$, *thiomethylene glycol*, is not known in the free state. The diethyl ether, $CH_2(SC_2H_5)_2$, b.p. 184°, sp.gr. 0·987 at 20°, is obtained by the treatment of sodium mercaptide with methylene iodide (Claesson, J. pr. Chem. [ii.] 15, 176).

Methylene sulphonic acid $CH_2(SO_3H)_2$, *Methane disulphonic acid*, forms very unstable needle-like crystals. Produced in small quantity by the action of sulphur trioxide upon ether (Liebig, Annalen, 13, 35; Strecker, *ibid.* 100, 199); by the oxidation of methylene thiocarbonate (Husemann, *ibid.* 126, 293); from chloroform and potassium sulphite solution at 180° or from iodoform and potassium sulphite at 150° (Strecker, *ibid.* 148, 92).

Preparation—Lactic acid or calcium lactate is heated with fuming sulphuric acid until sulphur dioxide begins to be evolved; the mixture is then neutralised with barium carbonate. It can also be prepared by heating 2 volumes of acetamide with 1 volume of fuming sulphuric acid (Buckton and Hofmann, Annalen, 100, 133). For salts *v.* Hofmann, Strecker, *l.c.*, also Monari (Ber. 1885, 1343).

Hexamethylenetetramine, *hexamethyleneamine, formamine, ammonio-formaldehyde, ammonaldehyde. cystamin, cystogen, formin, metramine, urisol, uritone, urotropine, vesalvine* $(CH_2)_6N_4$, is prepared by the action of ammonia on trioxymethylene (Butlerow, Annalen, 115, 322); from alcoholic ammonia and methylene chloride at 125° (Höland, *ibid.* 240, 225); or by passing formaldehyde vapour into a concentrated solution of ammonia, evaporating to a syrupy consistency and pouring into alcohol (Wohl, Ber. 1886, 1842). Commercial ammonium carbonate is dissolved in 40 p.c. formaldehyde solution, the solution is evaporated to dryness under reduced pressure and the residue is sublimed *in vacuô*, or recrystallised from absolute alcohol. It forms rhombohedral crystals from alcohol, is insoluble in ether, but readily in water and chloroform. Thioformaldehyde is produced by heating it with hydrogen sulphide. It is precipitated from its aqueous solution by bromine as an orange-red tetrabromide

$$C_6H_{12}N_4Br_4$$

which, when kept over potash, loses two atoms of bromine; the resulting dibromide melts at 198°-200°. This dibromide when boiled with water is decomposed into formaldehyde, water, ammonia, and hexamethylenetetramine. Hexamethylenetetramine is also precipitated from its solutions by mercuric chloride quantitatively. In the presence of ammonium salts it may be estimated by heating it with strong potash, by which it is unaffected, until all ammonia is expelled, then making acid and boiling to decompose the hexamethylene tetramine and subsequently making alkaline and estimating the ammonia in the usual way (Puckner and Hilpert, J. Amer Chem. Soc. 1908, 1471). The purity of a specimen is readily examined qualitatively by means of Nessler's solution, which shows the presence of ammonia and ammonium salts by the usual yellow colour or brown precipitate, and of formaldehyde by a precipitate of mercury (Wohlk, Zeitsch. anal. Chem. 1905, 765). Many compounds and derivatives of hexamethylene tetramine have been prepared and patented. The compounds with halogen pyrroles and aromatic sulphuric acids by Stange (Eng. Pat. 4804, 1899); with phenol and phenol mono- and poly- sulphuric acids and their halogen derivatives by the Chemische Fabriken vorm. Weiler-ter-Meer (D. R. P. 124231); basic compounds by Karl Hock (D. R. P. 139394); *cystopurin*, a compound of 1 mol. hexamethylenetetramine and 2 mols. sodium acetate by Bergell and Wülfing (Eng. Pat. 29093, 1906; U.S. Pat. 852993, 1907; Chem. Zentr. 1907, i. 487); the chloral, bromal, and butyl chloral derivatives by Lederer (Eng. Pat. 17693, 1897); the quinate by Wichmann and Gabler (U.S. Pat. 690804, 1902; Zimmermann, Eng. Pat. 14834, 1899); the salicylic acid compound by O. Imray (Eng. Pat. 22481, 1895); a powerfully astringent compound resulting from the condensation with tannin by H. E. Newton (Eng. Pat. 10790, 1898); 'ammonium compounds' by Farbenfabriken vorm. Baeyer & Co. (D. R. P. 164510); the borate by Aktien Gesellschaft für Anilinfabriken (Fr. Pat. 363764, 1906; U.S. Pat. 869636; Eng. Pat. 5039, 1906). In addition the following derivatives have been prepared: salts of inorganic acids and compounds with metallic salts by B. Grützner (Chem. Zentr. 1898, ii. 663); halogen derivatives by Horton (Ber. 1888, 1999), and Höhnel (Chem. Zentr. 1900, i. 409); bromo-iodides and chloroiodides by Mouneyrat (Compt. rend. 136, 1472); the chromate by K. A. Hofmann (Ber. 1906, 3181). Quaternary salts have been prepared by Hahn and Walter (Ber. 1921, 54 [B] 1531). The products of decomposition have been studied by Ischidzu and Inouye (Chem. Zentr. 1906, i. 1087), Grassi-Cristaldi; and Di Franco by the catalytic hydrogenation with reduced nickel has obtained trimethylamine, ammonia, and methane (*ibid.* 1907, i. 237).

Methylene tetramethyl diamine

$$CH_2[N(CH_3)_2]_2$$

is prepared from formaldehyde and dimethylamine (Henry). It boils at 85°, and has sp.gr. 0·7491 at 18·7°.

Methylene tetraethyl diamine $CH_2[N(C_2H_5)_2]_2$, b.p. 166°-169° (168° Henry). Formed by the action of trioxymethylene, 6·5 parts, upon diethylamine, 29·2 parts (Kolotoff, J. Russ. Phys. Chem. Soc. 17, 244). It is an unpleasant-smelling liquid, insoluble in water, but very soluble in alcohol; sp.gr. 0·8105 at 18·7° (Henry, Ber. 1893 (Ref.) 934).

Methylene tetrapropyl diamine

$$CH_2[N(C_3H_7)_2]_2$$

boils at 225°-230° with decomposition; sp.gr. 0·8014 at 18° (Henry).

Methylene thiocarbonate CH_2CS_3. A yellowish-white, amorphous powder insoluble in water, almost insoluble in alcohol, ether, or carbon disulphide, obtained by the action of methylene iodide upon sodium thiocarbonate in alcoholic solution (Husemann, Annalen, 126, 292). Is decomposed by ammonia into ammonium thiocyanate and methylene sulphide $(CH_2S)_3$.

Methylene thiocyanate $CH_2(CSN)_2$, m.p. 102°. From methylene iodide and potassium thiocyanate in alcoholic solution (Lermontoff, Ber. 1874, 1282). It forms needles or prisms which are almost insoluble in cold, moderately soluble in warm water, and easily soluble in alcohol or ether. By oxidation, *e.g.* by nitric acid, it yields methylene disulphonic acid.

Dimethylene dimethyl diamine

$$(CH_2)_2N_2(CH_3)_2$$

A crystalline non-volatile body obtained by passing trimethylamine and hydrogen through a heated tube (Romeny, Ber. 1878, 835).

Dimethylene diethyl diamine

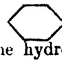
$$(CH_2)_2N_2(C_2H_5)_2$$

b.p. 205°-208°. Obtained by heating in a sealed tube a mixture of trioxymethylene with ethylamine (Kolotoff, J. Russ. Phys. Chem. Soc. 17, 231). An oily liquid with an unpleasant odour, soluble in cold water or in alcohol. Is decomposed by hydrochloric acid into trioxymethylene and ethylamine.

β-METHYLADIPIC ACID *v.* PIMELIC ACID.

METHYLAL *v.* SYNTHETIC DRUGS.

METHYLALLOXAN *v.* ALLOXAN.

METHYL ANILINE  $NH{\cdot}CH_3$. (1) Made by digesting aniline hydrochloride with methyl alcohol in an autoclave at 180°, adding milk of lime and steam-distilling. (2) By heating a mixture of aniline with methyl alcohol in presence of iodine at 220° (Knoll and Co. D. R. P. 250236). (3) By condensing aniline with formaldehyde and reducing the anhydroformaldehyde aniline ($(CH_2 : N{\cdot}C_6H_5)_3$) with zinc and sodium hydroxide (Geigy and Co., D. R. P. 75854). (4) By adding formaldehyde (40 p.c. solution) to a mixture of aniline and caustic soda containing zinc dust, heating and steam distilling (Morgan, Eng. Pat. 102834 of 1916). (*Cf.* Frankland, Challenger and Nicholls, Chem. Soc. Trans. 1919, 115, 198).

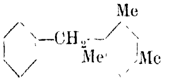
Methylaniline boils at 192°. Sp.gr. 0·976 at 15°. Yields *methylethylaniline* (b.p. 201°) on ethylation (Claus and Howitz, Ber. 1884, 17, 1324.

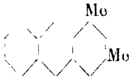
METHYL-ANTHRACENE AND OTHER ALKYL DERIVATIVES OF ANTHRACENE (*see also* articles on Aloes, Cochineal, Chrysophanic Acid, Cascara Sagrada, Indanthrene, Kermes, Rhubarb, Vat Dyes). In order to obtain the higher homologues of anthracene, it has been found necessary in most cases to resort to synthetical methods, as very few of these substances have been met with in coal tar.

The methods usually employed are the following:—

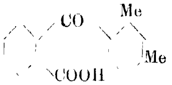
(1) Elimination of hydrogen from the hydrocarbons of the C_nH_{2n-14}, or C_nH_{2n-16} series, by passing them through red-hot tubes.

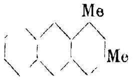
Benzyl mesitylene is thus converted into dimethylanthracene.



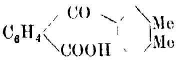


(2) By distilling *o*-ketonic acids with zinc-dust (Gresly, Annalen, 234–238); *m*-xyloyl-*o* benzoic acid yields *m* dimethylanthracene,

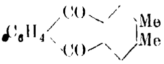




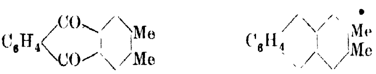
(3) By the action of sulphuric acid on *o*-ketonic acids (at about 125°), and subsequent reduction with zinc-dust and ammonia (Elbs, J. pr. Chem. 1890, 41, 1, &c.).



o-Xyloyl-*o*-benzoic acid



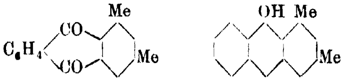
o-Dimethylanthraquinone.



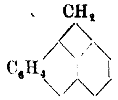
o-Dimethylanthracene.

This reaction cannot be successfully employed in a number of cases where one of the methyl groups is attached to the carbon atom next to the carbonyl group, as under these conditions anthracylene derivatives frequently result (*v.* Elbs, *l.c.* pp. 15–18).

Thus *m*-dimethylanthraquinone, on reduction with zinc dust and ammonia, yields *m*-dimethylanthracylene and not *m*-dimethylanthracene.



m-Dimethylanthranol.

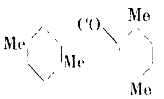


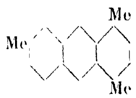
m-Dimethylanthracylene.

And similarly in a number of other cases.

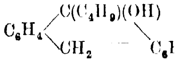
It should, however, be remarked that the results of a number of Elbs' analyses of these anthracylene derivatives agree only so very approximately that this explanation can scarcely be looked on as completely satisfactory.

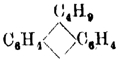
(4) By the prolonged boiling of some ketones. Thus di-*p*-xylyl ketone, when boiled for 6 hours under a reflux condenser yields (1,4,7) trimethylanthracene (Elbs and Olberg, Ber. 19, 409).



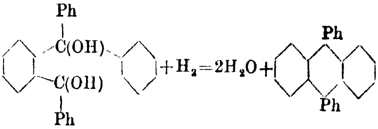


(5) The homologues of anthracene of the fromula $C_6H_4(C_2H(C_nH_{2n+1})C_6H_4$ are produced by boiling the alkylhydroanthranol with alcohol, hydrochloric acid, or picric acid. Thus *iso*butyl hydranthranol yields *iso*butylanthracene.



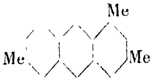


(6) Homologous arylanthracenes substituted in the γ position arise when the carbinols resulting from the action of magnesium aryl halogen compounds on anthraquinone and its derivatives are reduced. Thus diphenyl anthracene results when the corresponding carbinol is treated with zinc and acetic acid.

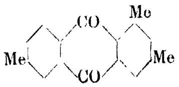


In their properties and reactions the homologues of anthracene behave very similarly to anthracene itself. On oxidation with chromic acid they yield corresponding anthraquinone derivatives, but in most cases the oxidation goes further and converts a portion of the anthraquinone into mono-, di-, or tricarboxylic acid, according to the number of side chains present, thus

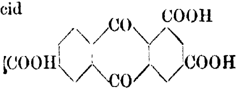
(1,3,6) Trimethylanthracene



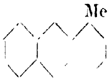
on oxidation yields first trimethylanthraquinone



and ultimately (1,3,6) anthraquinone tricarboxylic acid



α-Methyl anthracene



According to Birukoff (Ber. 20, 2069), α-methyl anthracene may be prepared by the distillation of methyl erythroxy anthraquinone with zinc-dust. O. Fischer and Sapper (J. pr. Chem. 1911, [ii.] 83, 201), obtained only a small yield of the substance in this manner; the main product was anthracene. The best method of preparation, according to these authors, consists in heating 4-chloro-1-methylanthraquinone with zinc-dust at a very low red heat. α-methylanthracene crystallises in long colourless needles, has m.p. 85°–86°, and is much more soluble in most solvents than anthracene or β-methylanthracene. Its solution in alcohol exhibits blue fluorescence. With picric acid, α-methylanthracene forms a compound crystallising in red needles, having m.p. 113°–115°.

9 : 10-*Dihydro-1-methylanthracene* is obtained by reduction of α-methylanthracene in boiling amyl alcoholic solution by means of sodium (Fischer and Ziegler, J. pr. Chem. 1912, [ii.] 86, 289). The substance is volatile in steam and crystallises in colourless needles, melting at 30°

4-*Chloro-1-methylanthracene* is obtained on boiling 4-chloro-1-methylanthraquinone with zinc-dust and aqueous ammonia. It melts at 112° and, unlike the corresponding quinone, does not part with halogen on distillation with zinc-dust.

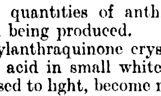
The *picrate* crystallises from benzene in dark red needles, m.p. 118°.

9 : 10-*Dihydro-4-chloro-1-methylanthracene* (Fischer and Ziegler, *l.c.*) is prepared by reducing 4-chloro-1-methylanthracene with hydrogen iodide in glacial acetic acid solution. It crystallises from methyl alcohol in colourless needles, melting at 47°–48°.

9 : 10-*Dihydro-9 : 10-dibromo-4-chloromethylanthracene* crystallised in greenish prisms from toluene and is obtained by the addition of bromine to a solution of 4-chloro-1-methylanthracene in carbon disulphide (Fischer and Ziegler, *l.c.*).

1-*Chloro-4-methylanthranol* is obtained by reduction of 4-chloro-1-methylanthraquinone by means of hydrogen iodide in boiling acetic acid solution. Bright yellow needles, m.p. 145°–146°, readily soluble in benzene and chloroform, more sparingly so in alcohol (Fischer and Ziegler, *l.c.*).

α-Methyl anthraquinone

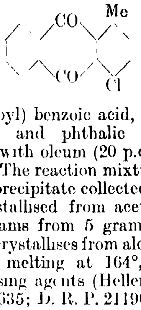


is readily prepared by oxidising α-methylanthracene with chromic acid in acetic acid solution, only small quantities of anthraquinone carboxylic acid being produced.

α-Methylanthraquinone crystallises from dilute acetic acid in small white needles, which, when exposed to light, become reddish-coloured. It melts at 170°–171°, is very readily soluble in alcohol or benzene, but difficultly soluble in glacial acetic acid.

It differs from its 4-hydroxy derivative in that it does not lose its methyl group on distillation with zinc-dust. Since α- and β-methylanthracene are obtained on submitting many natural products to zinc-dust distillation, it is of importance to be able to distinguish between them. α-Methylanthraquinone differs from the corresponding β- compound in turning red on exposure to light. Moreover it is oxidised by dilute nitric acid at 160° to anthraquinone-1-carboxylic acid, which develops a rose coloration when heated with soda lime. Under these conditions anthraquinone-2-carboxylic acid gives a blue colour.

4-*Chloro-1-methylanthraquinone*,

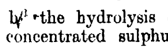


o-(*p*-Chlorotoluoyl) benzoic acid, prepared from *p*-chlorotoluene and phthalic anhydride, is heated at 100° with oleum (20 p.c. SO_3) for one to two hours. The reaction mixture is added to water and the precipitate collected, washed with alkali and crystallised from acetic acid. The yield is 4·4 grams from 5 grams of the acid. The substance crystallises from alcohol in slender yellow needles, melting at 164°, and is very stable to oxidising agents (Heller and Schülke, Ber. 1908, 41, 3635; D. R. P. 211967). A bromo-derivative (M.L.B., D. R. P. 259881) may be prepared in nitrobenzene solution. It melts above 300° and crystallises in orange needles from nitrobenzene. This substance is stated to dye cotton orange from a vat.

4-*Nitro-1-methylanthraquinone* (?) is obtained by treating 1-methylanthraquinone with concentrated nitric acid (Fischer and Ziegler, *l.c.*). It crystallises from acetic acid in glistening yellow needles, melting at 252°.

4-*Anilino-1-methylanthraquinone* may be prepared by heating 4-chloro-1-methylanthraquinone (2 grams) with aniline (12 grams) and dry sodium acetate (2 grams) at 185° during ten hours. It crystallises from alcohol in reddish-black needles, melting at 144°, and moderately readily soluble in chloroform, acetone and benzene. The corresponding *p*-toluidino-derivative occurs in dark red rods, m.p. 159°–160° (Grünthal and Ruthenberg, Ber. 1912, 45, 796).

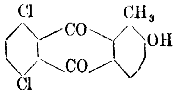
2-Hydroxy-1-methylanthraquinone



is obtained by the hydrolysis of its methyl ether with concentrated sulphuric acid. It crystallises from acetic acid in yellow needles which melt above 300°. Its red-violet potassium salt is sparingly soluble in water.

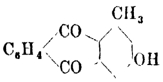
Methyl ether. This is the product of the action of sulphuric acid at 155° on 4′-methoxy-5′-methyl-2-benzoylbenzoic acid. It crystallises in canary-yellow needles from methyl alcohol and melts at 184°. The substance is soluble in acetic acid or ethyl alcohol and may be sublimed. It forms a monobromo- derivative, melting at 228°, and when dissolved in fuming nitric acid, yields a nitro-methoxy-methylanthraquinone which forms canary-yellow needles, melting at 179°. The latter on reduction with stannous chloride in alkaline solution is converted into the corresponding amino compound. This amino-methoxy-methyl anthraquinone separates from methyl alcohol in bright red needles of m.p. 187°. Acetamino-methoxy-methyl anthraquinone crystallises from acetic acid in brown needles, melting at 204°. On energetic nitration, 2-methoxy-1-methylanthraquinone yields a trinitro derivative (Bentley, Gardner and Weizmann, Chem. Soc. Trans. 91, 1626).

5:8-*Dichloro-2-hydroxy-1-methylanthraquinone*

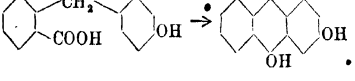


3 : 6 : Dichlorphthalic anhydride condenses with *o*-tolyl methyl ether in presence of aluminium chloride and the product is probably 3 : 6-dichlor-3′-hydroxy-2-*o*-toluoyl benzoic acid. This acid on heating with fuming sulphuric acid and boric acid, is converted to the quinone which separates from acetic acid as a yellow flocculent powder, decomposing at 249°. It should be remarked that in the above methyl hydroxy compounds, the methyl group may have the position 3 (Walsh and Weizmann, Chem. Soc. Trans. 97, 691).

3-Hydroxy-1-methylanthraquinone



This quinone has been synthesised by the following series of operations (Bistrzycki and Yssel de Schepper, Ber. 31, 2975). The condensation of phthalic anhydride and *m*-cresol yields a benzoyl benzoic acid which, on reduction, furnishes 4-hydroxy-2′-methyldiphenylmethane carboxylic acid. This compound, on treatment with sulphuric acid, is changed with loss of the elements of water into 1-methyl-3 : 10-dihydroxyanthracene thus :—

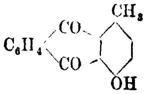


This anthracene derivative crystallises from alcohol in needles melting at 224°. Its diacetate forms microprisms from benzene and melts at 171°–173°. On oxidation with chromic acid in acetic acid solution, this diacetate yields the acetyl derivative of 3-hydroxy-1-methylanthraquinone. The derivative crystallises from alcohol in yellow needles. melting at 130°–135°, and on hydrolysis with alcoholic potash the parent quinone is produced.

3-Hydroxy-1-methylanthraquinone occurs in needles, sublimes at 200° and melts at 299°–300°. It dissolves in ammonia to an orange solution.

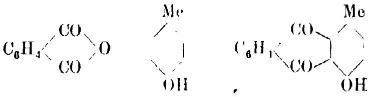
5 : 8 - *Dichloro* - 3 - *methoxy* - 1 - *methylanthraquinone* (Walsh and Weizmann, *l.c.*) is obtained in small yield by treatment of the benzoyl benzoic acid from dichlorphthalic anhydride and *m*-tolyl methyl ether with sulphuric acid. The yellow compound crystallises from acetic acid and decomposes at 236°.

4-Hydroxy-1-methylanthraquinone



(Methyl erythroxyanthraquinone).

is produced when a mixture of phthalic anhydride and *p*-cresol is heated with concentrated sulphuric acid (Birukoff, *l.c.*).



Preparation :—5 parts of phthalic anhydride, 2 parts of *p*-cresol, and 15 parts of concentrated sulphuric acid are heated to 160° for ten minutes, the product poured into water, the precipitate well washed with boiling water, and extracted with boiling dilute caustic potash solution. 4-Hydroxy-1-methylanthraquinone is obtained from the alkaline solution by the addition of hydrochloric acid in yellow flocks, which are readily purified by recrystallisation from glacial acetic acid The pure substance is thus obtained in beautiful dark-brown needles, melting at 175°.

This quinone may also be obtained by the hydrolysis of its methyl ether, either by means of acetic acid and hydrochloric acid at 100° under pressure or with concentrated sulphuric acid. Further, the condensation of phthalic anhydride and *p*-cresol is well effected by fusion with boric acid. A benzoyl benzoic acid results, and thus, by further treatment with sulphuric acid, yields the quinone (Bentley, Gardner and Weizmann, *l c.*).

4-Hydroxy-1-methylanthraquinone is almost insoluble in ammonia and sodium carbonate solution, readily soluble in caustic potash solution with a red coloration ; with baryta or lime-water insoluble brick-red lakes are produced. It dissolves in sulphuric acid with an orange-yellow colour, sublimes very easily, and in all its reactions, and also in its absorption spectrum, shows great similarity with erythroxyanthraquinone.

Fusion with potash converts it with difficulty into a colouring matter which is probably α-methylalizarin.

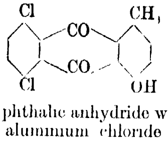
The *acetate* crystallises from acetic acid in yellow needles, which melt at 179°–180°.

Methyl ether. O. Fischer and Sapper (J. pr. Chem. 1911, [ii.], 83, 201) obtained this substance by the action of methyl alcoholic potassium hydroxide at 100° under pressure on 1-methyl-4-chloroanthraquinone. They described it as consisting of yellow needles of m.p. 128° and reddening under the action of light. Bentley, Gardner and Weizmann (*l c.*) condensed phthalic anhydride with *p*-tolylmethyl ether and so obtained 2′-methoxy-5′-methyl-2-benzoylbenzoic acid. The action of sulphuric acid at 150° on this compound led to the formation of the methyl ether of 4-hydroxy-1-methyl-anthraquinone, described as orange-yellow needles from methyl alcohol, melting at 171°.

3-*Nitro*-4-*hydroxy*-1-*methylanthraquinone* (?)

is the product of the nitration of 4-methoxy-1-methylanthraquinone (Fischer and Ziegler, J. pr. Chem. 1912, [ii.] 86, 292). It crystallises in glistening orange prisms from acetic acid and melts at 182°. It may also be obtained from 4-chloro-1-methylanthraquinone by nitration in presence of boric acid (Fischer and Rebsamen, Ber. 1914, 47, 464).

5 : 8-*Dichloro-4-hydroxy-1-methylanthraquinone*



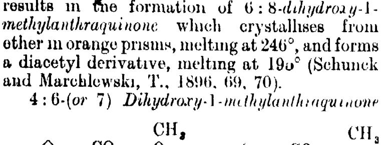
3 : 6 : Dichlorphthalic anhydride was condensed by means of aluminium chloride with *p*-tolyl methyl ether. The resulting 3 : 6 : dichloro-5′-hydroxy-2-toluoyl-benzoic acid was heated with fuming sulphuric acid (10 p.c. SO_3) in presence of boric acid for a few minutes at 130°. The quinone separates from acetic acid in micro-needles of m.p. 259°. Its brilliant red solution in concentrated sulphuric acid exhibits purple fluorescence. Its acetyl derivative forms lemon-yellow needles, melting at 181°.

When heated with sodium phenoxide and copper powder, one chlorine atom is replaced by phenoxyl.

2-*Nitro*-3 : 4-*dihydroxy*-1-*methylanthraquinone* is obtained by treating 4-chloro-1-methylanthraquinone with nitric acid first in the cold and then at 60°–70°. It crystallises from acetic acid in red needles, melting at 217°–218°, and yields a diacetyl derivative, yellow needles melting at 188°. The salts are intensely coloured and the potassium salt crystallises in bluish-violet needles. On reduction with stannous chloride and potassium hydroxide the corresponding aminohydroxymethylanthraquinone is obtained. This separates from benzene in dark red needles, melting at 285° (Fischer and Rebsamen, *l.c.*).

5 : 7-*Dihydroxy*-1-*methylanthraquinone* may be prepared by heating 3 : 5-dihydroxybenzoic acid (1 part) and *m*-toluic acid (4 parts) with sulphuric acid (25 parts) during ten hours at 110°. By crystallisation of the product from benzene the more soluble 6 : 8-dihydroxy-2-methyl anthraquinone, which is formed to some extent, is removed. In a similar way condensation of 3 : 5-dihydroxybenzoic acid and *o*-toluic acid results in the formation of 6 : 8-*dihydroxy*-1-*methylanthraquinone* which crystallises from ether in orange prisms, melting at 246°, and forms a diacetyl derivative, melting at 195° (Schunck and Marchlewski, T., 1896, 69, 70).

4 : 6-(*or* 7) *Dihydroxy*-1-*methylanthraquinone*

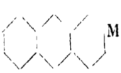


4-Hydroxyphthalic acid or its anhydride, when fused with boric acid and *p*-cresol, yields a benzoylbenzoic acid from which, by the further action of sulphuric acid, this quinone is obtained. The substance crystallises as a yellow powder from alcohol, and melts at 244°–246°.

A methyldimethoxyanthraquinone, which is probably, although not necessarily, the dimethyl ether of the above quinone, is obtained by condensing 4-methoxyphthalic anhydride with *p*-tolylmethyl ether by means of aluminium chloride and subsequently treating the benzoylbenzoic acid so produced with sulphuric acid (containing 60 p.c. SO_3) in presence of boric acid below 40°. The substance crystallises from acetic acid and melts at 141°. One methoxyl group is hydrolysed by the action of sulphuric acid at 110°.

4 : 5 : 6 (or 4 : 7 : 8) - *Trihydroxy*-1 - *methyl*-*anthraquinone* was obtained by Liebermann and Kostanecki (Annalen, 1897, 240, 304) by hydrolysis of its dimethyl ether, which is prepared by condensation of hemipinic acid and *p*-cresol in presence of sulphuric acid. The same authors prepared 5 : 6 : 7 - *trihydroxy*-1 - *methylanthraquinone* by condensation of *m*-toluic acid and gallic acid. This substance melts at 235°–240°, and gives a triacetyl-derivative, melting at 217°–218°. An isomeric methylanthragallol, namely, 6 : 7 : 8-*trihydroxy*-1-*methylanthraquinone*, golden yellow needles, melting at 297°–298° (triacetate, m.p. 208°–210°), is obtained by heating together equal parts of gallic acid and *o*-toluic acids at 130°–135° for 12 hours.

β-Methylanthracene



This hydrocarbon is found in varying quantities, together with anthracene and phenanthrene, in the fraction of coal tar which distils above 340°.

It may be synthetically prepared by the following reactions.

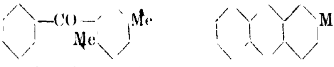
1. By passing the vapours of ditolylmethane (Weiler, Ber. 7, 1185) $CH_2(C_6H_4CH_3)_2$, ditolylethane (Fischer, *ibid.* 7, 1195),

$$CH_3\text{-}CH(C_6H_4CH_3)_2$$

or of oil of turpentine (Schultz, *ibid.* 10, 117) through a red-hot tube.

It is best in this reaction to employ ditolylethane, since the hydrocarbon from ditolylmethane is mixed with anthracene.

2. By boiling *p*-xylylphenylketone for several days on a reflux apparatus (Elbs, J. pr. Chem. 1890, 41, 3).



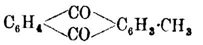
3. By the distillation of chrysophanic acid $C_{15}H_{10}O_4$, emodin $C_{15}H_{10}O_5$ (Liebermann, Annalen, 183, 163), colophonium, benzoe resin (Ciamician, Ber. 11, 273), chrysarobin $C_{30}H_{26}O_7$ (Liebermann and Seidler, Annalen, 212, 34) and methylquinizarine $C_{15}H_{10}O_4$ (Nietzki, Ber. 10, 2013) with zinc-dust.

According to Scholl (Monatsh. 1918, 39, 237), β-methylanthracene is best prepared synthetically by reduction of 2-methylanthraquinone with hydriodic acid and phosphorus. The melting-point of the substance so obtained is 206°–207°.

Preparation (Japp and Schultz, Ber. 10, 1049). The high boiling distillate of coal tar, known as crude phenanthrene, is freed from the greater part of the anthracene it contains by oxidation with potassium dichromate and sulphuric acid. The dark brown mass is extracted with hot alcohol, the well-cooled solution allowed to deposit as much anthracene and phenanthrene as possible, the mother-liquors which contain the methylanthracene evaporated and the residue repeatedly recrystallised from alcohol.

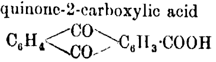
β-Methylanthracene crystallises from alcohol in pale yellow needles and melts at 202°–203°. It sublimes readily when heated continuously at 100°. It is difficultly soluble in ether, alcohol, glacial acetic acid, acetone, and light petroleum, readily soluble in benzene, chloroform, and carbon disulphide.

Oxidation with nitric acid converts it into methylanthraquinone



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot CH_3$$

Chromic acid oxidises it for the most part direct to anthraquinone-2-carboxylic acid

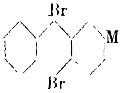


$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot COOH$$

Methylanthracene combines with picric acid, forming a compound which crystallises in large red needles; alcohol and water decompose this compound.

When sunlight acts on a benzene solution of the hydrocarbon, a dimeride, bis-β-methylanthracene, is formed (Orndorff and Megraw, Amer. Chem. J. 22, 152). It crystallises in rhombic crystals from toluene and melts at 228°. The substance is sparingly soluble and is converted on melting or solution in xylene into β-methylanthracene.

9 : 10-*Dibromo-2-methylanthracene*



is produced by treating methylanthracene in CS_2 with bromine; it crystallises from glacial acetic acid in yellow needles, m.p. 142°–143°.

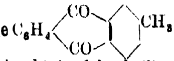
The position of the halogen atoms is proved by the oxidation of the substance to 2-methylanthraquinone.

Tetrabromomethylanthracene $C_{15}H_8Br_4$ is formed when dibromomethylanthracene is treated with bromine. It crystallises from toluene in yellow needles. Oxidation with nitric acid converts this compound into dibromomethylanthraquinone $C_{15}H_8Br_2O_2$.

The action of halogens on 2-methylanthracene has been studied by Fischer and Reinkober (J. pr. Chem. 1915, [ii.] 92, 49), who find that the products vary much according to the conditions employed. In benzene chlorination gives a mixture of mono- and dichloro-derivatives, whilst in chloroform the hexachloro-derivative, melting at 193°, is obtained. A mixture of mono- and decachloro-compounds is ultimately produced in a concentrated solution in carbon disulphide.

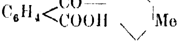
2-*Methylanthranol* (Limpach, Annalen, 1900, 237, 251). This compound, m.p. 100°, is produced by the action of sulphuric acid on *o*-(*p*-methylbenzyl) benzoic acid. It may also be obtained by reducing 2-methylanthraquinone with aluminium bronze in sulphuric acid solution (Bayer, D. R. P. 201542).

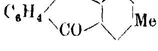
β-Methylanthraquinone



(O. Fischer, Ber. 8, 675) is obtained by boiling methylanthracene in alcoholic solution with nitric acid, or by carefully oxidising the hydrocarbon with CrO_3, in which latter case, however, considerable quantities of anthraquinone and anthraquinone carboxylic acid are also formed.

It has also been isolated from the by-products which accumulate in the manufacture of anthraquinone (Wachendorff and Zincke, Ber. 10, 1485; Börnstein, *ibid.* 15, 1820). This substance is identical with the methylanthraquinone which is obtained synthetically by heating *p*-methyl benzoylbenzoic acid with concentrated sulphuric acid (Gresly, Annalen, 234, 239).





This latter preparation is carried out in the following manner:—

The powdered acid is slowly added to 7 or 8 times its weight of concentrated sulphuric acid, and the mixture gradually heated until at the end of half an hour the temperature has risen to 120°–125°.

The clear dark brownish-red coloured solution is kept at this temperature for about an hour, allowed to cool and poured into much water. Steam is passed through the liquid for some time, the precipitate collected, washed well first with water, and lastly with dilute ammonia, dried, and the greenish-yellow mass purified by recrystallisation from a mixture of xylene and alcohol. Yield 70–75 p c. of theory.

β-Methylanthraquinone sublimes in yellow needles, m.p. 176°–177°; moderately soluble in ether, acetone, chloroform, or hot alcohol; difficultly soluble in glacial acetic acid and benzene.

1-*Chloro-2-methylanthraquinone.* 2-Methylanthraquinone (15 parts) is heated with nitrobenzene (25 parts), iodine (1 part), and sulphuryl chloride (15–20 parts) at 100° (D. R. P. 269249, 293156; Fr. Pat. 460,432).

3-*Chloro-2-methylanthraquinone.* This substance was first obtained by Heller and Schülke (Ber. 1908, 41, 3637) who condensed phthalic anhydride with *o*-chlorotoluene in presence of aluminium chloride and heated the resulting *o*-(*o*-chlorotoluoyl) benzoic acid with 20 p.c. oleum. Subsequently Ullmann and Dasgupta (Ber. 1914, 47, 557) described the same process with slight modifications and obtained a yield of 92–93 p.c. of the theory. This derivative crystallises from alcohol in colourless needles (H.S.) or plates (U.D.), melting at 212°–213° (compare also D. R. P. 205218, 211967).

3-*Bromo-2-methylanthraquinone* has been prepared from *o*-bromotoluene in an analagous manner by Grünthal and Ruthenburg (Ber. 1912, 45, 795). The yield was 85 p.c. of that theoretically possible. The compound occurs in long pale yellow needles and melts at 219°–220°. D. R. P. 216715 describes the preparation of an isomeride by direct bromination of 2-methylanthraquinone at 170°. This melts at 200°–202°, and in all probability hydrogen in the methyl group is displaced.

1-*Iodo-2-methylanthraquinone.* This derivative was obtained by Scholl (Ber. 1907, 40, 1691) in the course of his work on the synthesis of flavanthrene (*q v.*). It crystallises in brown leaflets, melting at 169°, and results from the action of potassium iodide on a solution of diazotised 1-amino-2-methylanthraquinone.

Dibromo-2-methylanthraquinone, m.p. 140°, may be obtained by brominating *o*-(*p*-toluoyl) benzoic acid and subsequently closing the ring in the usual manner.

Dibromomethylanthraquinone is obtained by the action of bromine at 130°–140° on *β*-methylanthraquinone. It is colourless and melts at 219°–220° (O. Fischer, J. pr. Chem. 1909, [ii.] 79, 555).

ω-Dichloro-β-methylanthraquinone is obtained by chlorination of methylanthraquinone. The substance melts at 200° and is converted by the action of sulphuric acid (66° Baumé) at 130° into *β*-anthraquinone aldehyde (Badische Anilin und Soda Fabrik, D. R. P. 174984).

3-*Chloro-2-dibromomethylanthraquinone* is obtained in 91 p.c. yield by the bromination of 3-chloro-2-methylanthraquinone in closed vessels at 160°–170° during five hours. The substance crystallises from toluene in hexagonal leaflets, melting at 210°–211° (Ullmann and Dasgupta, *l.c.*).

Methylanthraquinone disulphonic acid (O. Fischer, *l.c.*) $C_{15}H_8(HSO_3)_2O_2$.

Preparation. — Methylanthraquinone is heated with 5–6 parts of fuming sulphuric acid for several hours at 250°–270°. The alkali salts and the barium and calcium salts of this acid are soluble in water. Fusion with potash converts the acid into methylalizarin.

Nitromethylanthraquinone

$$C_{15}H_9NO_4 \text{ or } CH_3{\cdot}C_{14}H_6(NO_2)O_2$$

Preparation.—Methylanthraquinone (2 parts) is dissolved in concentrated H_2SO_4 (12–14 parts), and to the resulting solution KNO_3 (1 part) is slowly added. The product after standing 24 hours is carefully mixed with water, the precipitate collected, and extracted repeatedly with alcohol until the filtrate is only slightly yellowish-coloured. The resulting nitromethylanthraquinone is purified by recrystallisation from acetic acid (Römer and Link, Ber. 16, 695), from which solvent it is obtained in yellow needles melting at 269°–270°. It is difficultly soluble in alcohol, ether, benzene, chloroform, glacial acetic acid, and ethyl acetate, readily soluble in nitrobenzene. It dissolves in sulphuric acid, producing a yellow solution which on warming turns brown. Water precipitates from this solution a purple precipitate, which dissolves in alkalis with a violet-blue colour. Nitromethylanthraquinone sublimes in small almost colourless needles. It is not decomposed by boiling caustic potash solution.

1 : 5-*Dinitro-2-methylanthraquinone.* Together with the 1 : 8-isomeride this compound is prepared by the action of a mixture of sulphuric and nitric acids at 60°–70° in 2-methylanthraquinone. The concentration and amount of nitric acid is in this case greater than in the experiment described above. The 1 : 5-derivative is more sparingly soluble than is the 1 : 8-isomeride in boiling glacial acetic acid. It is bright yellow and melts at 251°–252°. 1 : 8-Dinitro-2-methylanthraquinone melts at 189°–190° (Schaarschmidt and Stahlschmidt, Ber. 1912, 45, 3454).

Aminomethylanthraquinone,

$$CH_3{\cdot}C_{14}H_6(NH_2)O_2,$$

is readily produced by the reduction of nitromethylanthraquinone with $SnCl_2$ (Römer and Link, *l.c.*). The freshly precipitated nitro compound is added in small quantities at a time to a dilute solution of $SnCl_2$ in KOH, and the product heated nearly to boiling. The resulting precipitate, which must dissolve completely in excess of cold HCl, is purified by recrystallisation from dilute HCl. The reduction of nitromethylanthraquinone may also be readily effected by means of a hot aqueous solution of sodium sulphide.

Aminomethylanthraquinone crystallises in glittering red needles which melt at 202°, and sublimes on heating in long dark red needles. It is almost insoluble in water, readily soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid. Boiling with hydriodic acid and phosphorus converts it into aminomethylanthranol; at 150°, however, aminomethylanthracenedihydride $CH_3{\cdot}C_{14}H_{10}NH_2$ results.

The *acetyl-derivative*,

$$CH_3{\cdot}C_{14}H_6O_2NH(C_2H_3O),$$

crystallises from glacial acetic acid in yellow needles, m.p. 176°–177.°

An isomeric aminomethylanthraquinone, probably 2-amino-6- (or 7) methylanthraquinone is prepared from amino-*p*-toluoylbenzoic acid by heating with 80 p.c. sulphuric acid at 200°. It crystallises in brick-red needles and melts at 175° (D. R. P. 134917).

1 : 3-*Diamino-2-methylanthraquinone.* 1 : 3-Dinitro-2-*p*-toluoylbenzoic acid is reduced to the corresponding diamino-acid by means of iron and dilute acetic acid. The conversion of the latter to an anthraquinone derivative occurs with unusual facility and it suffices to heat the substance with acetic acid. The diaminomethylanthraquinone crystallises in yellowish-red needles which melt at 273°–276° (D. R. P. 205036).

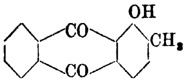
1 : 4-*Diamino-2-methylanthraquinone* crystallises from alcohol in dark violet bronzy needles melting at 252°. It is obtained from the lactam of 2 : 5-diamino-*p*-toluoylbenzoic acid by heating with 5 p.c. oleum at 180° (D. R. P. 260899).

1 : 5-*Diamino-2-methylanthraquinone* and 1 : 8-diamino-2-methylanthraquinone are obtained by the reduction of the corresponding nitro-derivatives (*vide supra*) with sodium sulphide. The former crystallises in red needles from acetic acid and melts at 201°–202°, and the latter separates from toluene in brown-red needles, melting at 206°–208°.

A *triaminomethylanthraquinone* of unknown constitution has been described (D. R. P. 205036).

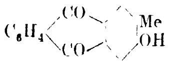
1-*Bromoamino-2-methylanthraquinone* is the first product of the action of bromine on 1-amino-2-methylanthraquinone. It crystallises in brownish-red needles, melting at 215°–216° (D. R. P. 131402). Further, a considerable number of nuclear substituted chloro- and bromo-amino- and diamino-methylanthraquinones have been mentioned (D. R. P. 131402 and 205218), but these are of unknown constitution. It is stated that certain substances of this type may be employed for the preparation of sulphurised vat-dyes.

1-Hydroxy-2-methylanthraquinone (Weizmann, Bentley and Gardner, *l.c.*)

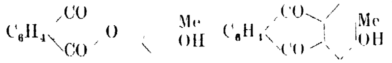


Phthalic anhydride condenses with ortho-cresol in presence of boric acid at 170° and yields 2′-hydroxy-3′-methyl-2-benzoylbenzoic acid. The yellow solution of this substance in concentrated sulphuric acid goes red on heating and yields on dilution this hydroxyanthraquinone. It forms yellow needles on crystallisation from acetic acid and melts at 184°–185°.

3-Hydroxy-2-methylanthraquinone

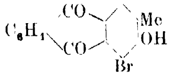


Preparation (Fraude, Annalen, 202, 613).—By heating 2 parts of *o*-cresol, 3 parts phthalic anhydride, and 100 parts of sulphuric acid at 160° for two days. The product is poured into water, extracted repeatedly with ether; the ether distilled off, the residue dissolved in dilute soda, acidified with HCl, and the precipitate purified by sublimation and recrystallisation from alcohol.



Hydroxymethylanthraquinone melts at 260°–262°, is readily soluble in alcohol, ether, and acetic acid; it dissolves in alkalis, also in lime and baryta water, forming a dark reddish-brown solution. When strongly heated it sublimes in golden-yellow leaflets.

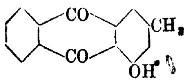
Bromohydroxymethylanthraquinone



is obtained by heating 4 parts of dibromo-*o*-cresol phthaleine ($C_{22}H_{16}Br_2O_4$) with 1 part of phthalic anhydride and 200 parts of sulphuric acid at 150° for five hours.

Small yellow needles, m.p. 205°. Fusion with potash converts this substance into α-methylalizarin.

4-Hydroxy-2-methylanthraquinone.



Bentley, Gardner and Weizmann (*l.c.*) obtained this quinone in a manner analogous to the preparation of 1-hydroxy-2-methylanthraquinone, by substituting *m*- for *o*-cresol. It melts at 178° and consists of yellow needles which are crystallised from acetic acid. A quinone probably identical was obtained by Römer and Link (Ber. 16, 700) from the aminomethylanthraquinone described above.

Preparation.—Aminomethylanthraquinone is dissolved in sulphuric acid, and solution mixed with small quantities of water until the resulting precipitate becomes reddish-coloured.

The well-cooled product is slowly mixed with a solution of KNO_2 until the precipitate becomes light yellow and free nitrous acid is evolved, then an equal volume of water is added and the whole heated to boiling.

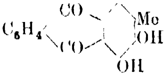
The precipitate is collected, dissolved in boiling dilute caustic potash solution, precipitated with HCl, and recrystallised from alcohol.

Hydroxymethylanthraquinone crystallises from alcohol in orange-yellow needles which melt at 177°–178°, and sublimes in long thin yellow plates when carefully heated. It is almost insoluble in water, difficultly soluble in alcohol, readily soluble in ether, and benzene. Cold caustic potash solution dissolves it sparingly.

Fused with potash a small quantity of a colouring matter is produced which dissolves in alkalis with colorations similar to those produced by alizarin. Hydroxymethylanthraquinone, if freshly precipitated, dissolves in boiling lime or baryta water, but is insoluble in sodium carbonate or a solution of alum. Its alcoholic solution is not precipitated by alcoholic lead acetate.

The *acetate*, $CH_3{\cdot}C_{14}H_6O_2(C_2H_3O_2)$, crystallises from alcohol in orange-yellow plates which melt at 177°.

Dihydroxymethylanthraquinone (α-methylalizarin),



is readily prepared by fusing methylanthraquinonedisulphonic acid (O. Fischer, *l.c.*), hydroxymethylanthraquinone, or bromohydroxymethylanthraquinone (Fraude, Annalen, 202, 166) with potash. The mass is dissolved in water, acidified with HCl, and the precipitate purified by sublimation. Orange-yellow needles, m.p. 250°–252°, moderately soluble in alcohol, ether, and acetone. The calcium and barium salts are insoluble blue precipitates.

The absorption spectrum of a solution of this substance in concentrated sulphuric acid is represented in Fig. 1.

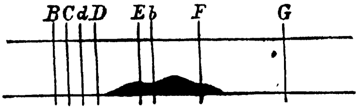
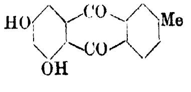


Fig. 1.

It corresponds very closely with that of alizarin itself (Liebermann and Kostanecki, Ber. 19, 2330). Methylalizarin dyes mordanted cloth similarly to alizarin, but according to some authorities the tinctorial power of methylalizarin is much inferior to that of alizarin, hence the introduction of this substance into artificial alizarin is avoided by the alizarin manufacturer as much as possible.

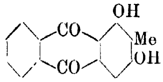
Methylpurpuroxanthins.

5 : 7-*Dihydroxy-2-methylanthraquinone*



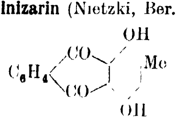
3 : 5-Dihydroxybenzoic acid (4 grams) and *p*-toluic acid (15 grams) are heated to 110° with sulphuric acid (200 grams) during three hours. The compound melts at 267° and forms a *diacetyl* derivative which crystallises in yellow needles, m.p. 165°–167° (Marchlewski, T., 1893, 63, 1142).

1 : 3-*Dihydroxy-2-methylanthraquinone*

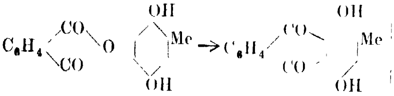


2 : 6-Dihydroxy-*p*-toluic acid (4 grams) and benzoic acid (15 grams) are heated together with sulphuric acid (200 grams) at 110°–120° for fifteen hours. The substance crystallises from benzene in orange needles, melting at 290°. (*Diacetate*, m.p. 217°–218°) (Schunck and Marchlewski, T., 1894, 65, 183.).

Methylquinizarin (Nietzki, Ber. 10, 2012)



This isomeride of methylalizarin is produced by heating a mixture of hydrotoluquinone and phthalic anhydride with 8–10 parts of sulphuric acid at 130°–150° for two to three hours. The product is treated with water, the precipitate repeatedly extracted with boiling water, and purified by recrystallisation from benzene



Methylquinizarin crystallises in long fine bent needles which melt at 160° and sublime with slight decomposition. The solutions in ether and alcohol are fluorescent. Distilled with zinc-dust methylanthracene is formed.

The absorption spectrum of methylquinizarine dissolved in sulphuric acid is represented in Fig. 2—

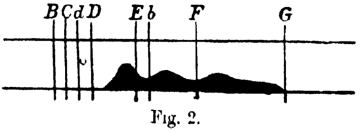
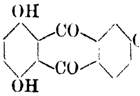


Fig. 2.

and is very closely allied to that of quinizarin itself.

Methylquinizarin when treated with acetic anhydride yields a *diacetate* $C_{15}H_8(C_2H_3O)_2O_4$, which crystallises in yellow needles, m.p. 185°.

5 : 8-**Dihydroxy**-2-**methylanthraquinone** (von Niementowski, Ber. 33, 1634)



This substance is prepared by heating together equimolecular quantities of 1-methyl-3 : 4-phthalic anhydride and hydroquinone with 6 parts of concentrated sulphuric acid for 5 to 10 hours at 140°–160°. It forms orange leaflets from alcohol mixed with benzene, or it may be crystallised from a large quantity of alcohol and obtained in beautiful ruby-red needles. It has the curious property of melting at 165°, resolidifying and melting again at 175°. The sublimed quinone melts at 175°. The solution in dilute caustic soda is violet-red.

Diacetyl derivative.—This is readily produced by the action of sodium acetate and acetic anhydride. It crystallises from benzene, is intensely yellow, and melts at 204°.

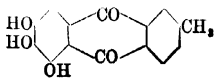
6 : 7-**Dihydroxy**-2-**methylanthraquinone** and 5 : 6- (or 7 : 8) **dihydroxy**-2-**methylanthraquinone** (Niementowski, *l.c.*).

The 6 : 7-dihydroxy compound is the main product when catechol is substituted for hydroquinone in the above preparation. It crystallises from acetic acid in yellow micro-needles and melts with decomposition at 320°–340°. Its diacetate forms straw-yellow needles from alcohol, m.p. 208°. The 5 : 6- (or 7 : 8) dihydroxy compound is produced in small quantities in the same reaction. It crystallises from a little benzene in orange-red needles and melts and sublimes at 216°. Its diacetate crystallises from alcohol in groups of transparent yellow needles ; m.p. 176°.

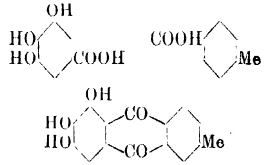
4 : 6- (or 7 :) **Dihydroxy**-2-**methylanthraquinone** (Bentley, Gardner, and Weizmann, *l.c.*).

4-Hydroxyphthalic anhydride and *m*-cresol, when fused with boric acid at 180°, yield a benzoylbenzoic acid in which the cresolic hydroxyl is in the ortho- position to carboxyl. With fuming sulphuric acid the substance condenses to the quinone, which separates from glacial acetic acid as a yellow crystalline powder of m.p. 284°.

β-**Methylanthragallol**, 5 : 6 : 7-**trihydroxy**-2-**methylanthraquinone**



Formation.—By heating a mixture of gallic acid and *p*-toluic acid to 130° (Cahn, Annalen, 240-284) :



Sublimes in orange-red needles, m.p. 275°. Its other properties are very similar to those of anthragallol itself. The absorption spectrum of its solution in sulphuric acid is shown in Fig. 3.

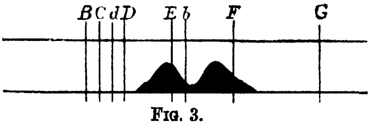
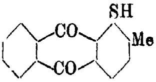


Fig. 3.

2-Methylanthraquinone-1-mercaptan



1-Amino-2-methylanthraquinone is converted into the mercaptan by diazotisation and treatment with potassium xanthogenate (Gattermann, Annalen, 1912, 393, 155). The substance crystallises from acetic acid in yellow needles which melt at 193°–194°. The following derivatives may be mentioned: Disulphide, yellow needles, m.p. 247°; methyl thioether, orange-red needles, m.p. 124°; sulphone from the methyl thioether, yellowish-red plates, m.p. 198°; ethyl thioether, orange-red leaflets, m.p. 99°; benzyl thioether, orange-red needles, m.p. 139°.

Miscellaneous dyes derived from β-methylanthraquinone.—The more important dyestuffs derived from methylanthraquinone directly or indirectly are treated in other sections of this work (*e.g.* Flavanthrene, Pyranthrene, certain Algol colours, Indanthrene Red BN, and many others), and the compounds here included are for the most part of unknown constitution.

Anthraflavone G (Bad. D. R. P. 199756, 1905. Schultz, No. 759) is obtained by heating 2-methylanthraquinone with concentrated alcoholic potassium hydroxide at 150°–170°. The product is poured into water and oxidised by means of hypochlorite. It is a yellowish-green powder which can be sublimed and gives a red-violet solution in sulphuric acid. It is a greenish-yellow vat dyestuff.

Cibanone Orange R (D. R. P. 209231, 209232; Schultz, No. 792). 2-Methylanthraquinone is fused with sulphur and the product oxidised. This orange cotton dyestuff is a red-brown powder.

Cibanone Brown B (D. R. P. 204958; Schultz, No. 868) is similarly obtained from 1-amino-2-methylanthraquinone by heating with sulphur. It is a brown-black powder and dyes cotton brown from a vat.

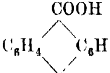
Cyananthrol R (B) (D. R. P. 131873; Schultz, No. 859) is a reddish-blue acid dyestuff for wool or silk. It is stated to be a derivative of methylanthraquinone.

Cyananthrol G (B) (D. R. P. 132622; Schultz, No. 860) is a similar dyestuff giving greenish-blue shades.

A brown dyestuff for cotton is said to be prepared by the addition of aluminium powder to a solution of β-methylanthraquinone in sulphuric acid at 20°–40°, the mixture being subsequently heated at 100°–120° (D. R. P. 203436). An orange sulphur dyestuff is obtained from β-methylanthraquinone or ω-chloro-β-methylanthraquinone (D. R. P. 223176) by heating with sulphur and then sulphuric acid, the product being finally oxidised by means of sodium hypochlorite. The thionation of 3-chloro-2-methyl-anthraquinone leads to the production of an orange-yellow vat dyestuff (D. R. P. 213506).

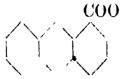
ω-Dibromo-2-methylanthraquinone heated with copper powder in nitrobenzene solution gives rise to a vat dyestuff (D. R. P. 267546) which may be 1 : 2 : 5 : 6-diphthaloylanthracene. ω-Dichloro-2-methylanthraquinone gives a yellow vat dyestuff, when condensed with thiourea (D. R. P. 241805) and other dyestuffs of a similar type are known, for example, that from 2-hydrazinoanthraquinone and anthraquinone-2-aldehyde or ω-dichloro-2-methylanthraquinone (D. R. P. 240520, 241786).

Considerable confusion exists in the literature with respect to the anthracene and anthraquinone carboxylic acids.

Anthracene-10-carboxylic acid (Liebermann, Graebe, Ber. 2, 678)  $\mathrm{C_6H_4}\overset{\mathrm{COOH}}{\Diamond}\mathrm{C_6H_4}$. The chloride of this acid is produced by heating anthracene with $COCl_2$ to 180°–200°.

The acid crystallises from alcohol in long, silky, pale yellow needles, which melt at 206° with decomposition. It is almost insoluble in cold water, readily soluble in alcohol. On distillation with soda lime it decomposes into CO_2 and anthracene. The salts are mostly soluble in water.

Anthracene-1-carboxylic acid

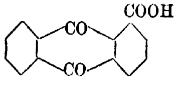


The nitrile of this acid is produced by distilling sodium anthracene α-monosulphonate with potassium cyanide (Liebermann and Pleus, Ber. 37, 646; see also Liebermann and Rath, *ibid.* 8, 246, and Dienel, *ibid.* 39, 926). The nitrile crystallises from alcohol in yellow leaflets, m.p. 126°, and is slowly hydrolysed by alcoholic potash with formation of the potassium salt of anthracene-1-carboxylic acid.

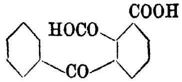
The acid may also be prepared by the reduction of anthraquinone-1-carboxylic acid with zinc-dust and ammonia (Graebe and Blumenfeld, *ibid.* 30, 1118). The acid forms yellow needles or prisms on crystallisation from alcohol and melts at 245°. It sublimes undecomposed in needles, is sparingly soluble in benzene and ether, readily soluble in alcohol and glacial acetic acid, insoluble in water. Distillation with soda lime decomposes it into CO_2 and anthracene. Chromic acid oxidises it to anthraquinone carboxylic acid $C_{15}H_8O_4$. The acid and its salts possess a blue fluorescence; the latter are mostly readily soluble in water. The Ba and Ca salts dried at 130° are yellow amorphous powders. The Pb salt is a flocky precipitate.

The amide of the acid is produced by the action of ammonia on the yellow oily chloride. It crystallises from alcohol and melts at 260° (Graebe, Blumenfeld), 256° (Dienel).

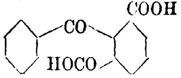
Anthraquinone-1-carboxylic acid



This acid is prepared by oxidising 1-methylanthracene with chromic acid (Liebermann and Bischoff, Ber. 13, 49), or by the hydrolysis of its nitrile (see below). A method which leaves no doubt as to its constitution has also been employed (Graebe and Leonhardt, Annalen, 290, 231; Graebe and Blumenfeld, Ber. 30, 1115). Hemimellitic anhydride and benzene in presence of aluminium chloride yield a mixture of 3-benzoylphthalic acid



and 2-benzoyl*iso*phthalic acid



Each of these acids, when heated with sulphuric acid at 145°–150°, is changed to anthraquinone-1-carboxylic acid.

Probably the most convenient method of preparation is that described by Ullmann and Schalk (Annalen, 1912, 388, 203), who apply the Sandmeyer reaction to α-aminoanthraquinone. The intermediately produced nitrile (see below) is hydrolysed by means of hot concentrated sulphuric acid mixed with one-third of its volume of water, and the over-all yield is about 70 p.c. of the theory.

It crystallises from glacial acetic acid in long pale yellow needles, which melt at 293°–294°. With caustic potash and zinc-dust, it develops a blood-red coloration. The barium salt is sparingly soluble. Its methyl ester is sparingly soluble in cold methyl alcohol and has m.p. 189°. The ethyl ester from the acid and alcoholic hydrochloric acid has m.p. 169°.

Nitrile (Dienel, Ber. 39, 926). This derivative is obtained by the distillation of sodium anthraquinone α-sulphonate with potassium cyanide, by oxidising the nitrile of anthracene-1-carboxylic acid, or by the method already described above. It forms gold-yellow leaflets of m.p. 216°–217°.

The amide has m.p. 280°.

β-Chloroanthraquinone-α-carboxylic acid has been obtained by the oxidation fo β-chloroaceanthrenequinone by means of chromic acid in acetic acid solution. It forms yellow needles, melting at 244°–246°. α-Chloroanthraquinone-α-carboxylic acid, m.p. 205°, is similarly obtained from α-chloroaceanthrenequinone (Butescu, Ber. 1913, 46, 213).

4-Chloroanthraquinone-carboxylic acid. 4-Chloro-1-methylanthraquinone is oxidised by means of nitric acid at 195°. The substance crystallises in yellow needles from ethyl acetate and melts at 228°-229° (Heller and Schulke, Ber. 1908, 41, 3636). Alternatively (D. R. P. 259365) chlorine is introduced into a solution of 4-chloro-1-methyl-anthraquinone in nitrobenzene at 160°-170°.

5 : 8-*Dichloroanthraquinone-1-carboxylic acid.* This acid is obtained when anthraquinone-1-carboxylic acid dissolved in fuming sulphuric acid is chlorinated at 125° in presence of iodine. It crystallises from acetic acid in needles, melting at 241° (D. R. P. 255121).

4 : 8-*Dichloroanthraquinone-1-carboxylix acid* is the oxidation product obtained from 1 : 5-dichloroacoanthrenequinone (Butescu, *l.c.*); m.p. 250°. Similarly the 4 : 5-*dichloroanthraquinone-1-carboxylic acid* is obtained from 1 : 8-dichloroacoanthrenequinone. It crystallises in yellow needles and melts at 240°.

2-*Bromoanthraquinone-1-carboyxlic acid.* The application of the Sandmeyer reaction to 2-bromo-1-aminoanthraquinone gives good results (Ullmann and Schalk, *l.c.*). The acid obtained by hydrolysis of the corresponding nitrile crystallises from acetic acid in yellow octahedra, which melt at 292°.

5-*Nitroanthraquinone-1-carboxylic acid.* Anthraquinone-1-carboxylic acid (10 grams) is heated on the steam bath with conc. sulphuric acid (100 c.c.) and nitric acid (6 c.c. D=1·4) during two hours. The derivative crystallises from acetic acid in yellow lamellæ which decompose above 330° (Ullmann and Schalk, *l.c.*). An isomer of this substance has been described by Fischer and Ziegler (*l.c.*), who oxidise the nitration product of α-methylanthraquinone. There is little doubt that these substances belong to the 1 : 4-series. The nitro-acid is sparingly soluble in sulphuric acid and decomposes at 270°.

4-*Aminoanthraquinone-1-carboxylic acid.* 1 : 4-Diaminoanthraquinone is semi-diazotised and converted into the amino-cyanide by treatment with cuprous cyanide at 30°. Hydrolysis of the product is effected by means of 10 p.c. soda at 150°. The substance crystallises in long dark brown needles, decomposing at 246°–248° (Gattermann, Annalen, 1912, 393, 176).

5-*Aminoanthraquinone-1-carboxylic acid* is prepared by the reduction of the corresponding nitro-acid (*vide supra*) with sodium sulphide. It forms dark red leaflets and decomposes at 277°. What should be the same substance was prepared by Gattermann (*l.c.*) from 1 : 5-diaminoanthraquinone by semi-diazotisation treatment with cuprous cyanide and hydrolysis. Prepared in this way, however, the substance is stated to crystallise in red prisms, melting at 265°.

β-Methylanthraquinone-1-carboxylic acid has been obtained by Butescu (*l.c.*) by oxidation of β-methylaceanthrenequinone with chromic acid. The bright yellow needles melt at 295°.

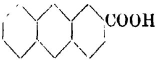
3-*Methylanthraquinone-1-carboxylic arid* is produced from 1 : 3-dimethylanthraquinone by oxidation with chlorine (D. R.P. 239365). It melts at 246°-147°.

Anthraquinone aldehydes.

4,*Chloroanthraquinone-1-aldehyde* is obtained by the oxidation of 4-chloro-1-methylanthraquinone by means of manganese dioxide in sulphuric acid solution (D. R. P. 267081). It melts at 210°.

Anthraquinone-2-aldehyde is the product of the hydrolysis of ω-dichloro-2-methylanthraquinone with sulphuric acid (66° Bé.) during five to six hours at 130° (D. R. P. 174984). It is also prepared by the oxidation of 2-methylanthraquinone by means of manganese dioxide and sulphuric acid (D. R. P. 267081) and by ring closing of ω-dibromo-2-*p*-toluoylbenzoic acid (D. R. P. 293981).

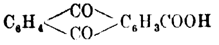
Anthracene-2-carboxylic acid.



The nitrile of this acid is obtained (together with a small quantity of the nitrile of the 1-acid) by distilling sodium anthracene sulphonate (from the acid obtained by the reduction of anthraquinone sulphonic acid) with potassium ferrocyanide (Liebermann and Bischoff, Ber. 13, 47).

The nitriles are decomposed by boiling with KOH, and the acids separated by means of their barium salts; that of the 1-acid being readily soluble in water, whereas barium anthracene 2-carboxylate is very sparingly soluble.

The same acid is produced by the reduction of anthraquinone-2-carboxylic acid


$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}C_6H_3COOH$$

with zinc-dust and ammonia (Börnstein, Ber. 16, 2610).

Anthracene-2-carboxylic acid crystallises from alcohol in small yellow plates, which melt at about 280°, and sublime at a higher temperature in plates. It is sparingly soluble in $CHCl_3$, almost insoluble in CS_2 and benzene, less soluble in alcohol and glacial acetic acid than the β-acid. The alcoholic solution possesses an intense blue fluorescence. Reduction with sodium amalgam or hydriodic acid converts this acid into three acids, $C_{15}H_{12}O_2$, $C_{15}H_{11}O_2$, and $C_{15}H_{16}O_2$. Chlorine led into the solution in $CHCl_3$ produces first γ-chloranthracene carboxylic acid and then dichloranthracene (m.p. 209°). Bromine behaves similarly.

The *Sodium salt* is difficultly soluble in cold water, and crystallises in glittering flakes. The solutions fluoresce blue.

The *Barium salt* is almost insoluble in cold water, and only very sparingly soluble in hot.

The *Methyl ester* (Behla, Ber. 20, 703)

$$C_{15}H_9O_2CH_3$$

crystallises in yellow prisms; m.p. 111°.

The *Ethyl ester* (Liebermann, Bischoff, Ber. 13, 49) $C_{15}H_9O_2C_2H_5$ melts at 134°, and is readily soluble in alcohol. Both these salts distil without decomposition.

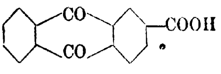
The *Chloride* (Börnstein, *l.c.*) $C_{15}H_9OCl$ crystallises from benzene in yellow warts; m.p. not given. Readily soluble in alcohol, ether, $CHCl_3$ and CS_2. Decomposed only by boiling water.

The *Amide* $C_{15}H_9ONH_2$ crystallises from glacial acetic acid in plates; m.p. 293°–295°. Insoluble in water, SC_2, CHC_3, or benzene. Difficultly soluble in alcohol. The solutions fluoresce blue.

γ-Chloroanthracene carboxylic acid (Behla, *l.c.*) (*v. supra*) crystallises from benzene in needles; m.p. 258°–259°, being at the same time decomposed into chloranthracene and CO_2.

γ-Bromoanthracene carboxylic acid (Behla, *l.c.*) crystallises from alcohol in long, greenish-yellow needles; melts at 266°, being converted into CO_2 and bromoanthracene.

Anthraquinone-2-carboxylic acid



is produced by oxidising 2-methylanthracene or the corresponding quinone or carboxylic acid (Liebermann, Rath, Ber. 8, 248). It may also be obtained by the oxidation of anthranol β-carboxylic acid with potassium permanganate in alkaline solution (Limpricht, Annalen, 309, 122).

According to the Höchster Farbwerke (D. R. P. 80407), it is conveniently prepared by heating benzophenone-2:4′-dicarboxylic acid with sulphuric acid.

Preparation.—Methylanthraquinone (1 part) is dissolved in concentrated sulphuric acid (6 parts), mixed then with water (1 part), and $K_2Cr_2O_7$ (2½ parts) slowly added. The mass is warmed to 110°–120° for a short time, filtered, the precipitate washed with water and boiled out with dilute ammonia. The excess of ammonia is evaporated off, the solution filtered, and precipitated with HCl (Börnstein, Ber. 16, 2609; *v.* also Liebermann and Glock, *ibid.* 17, 888).

Anthraquinone-2-carboxylic acid crystallises from alcohol in yellow prisms, which melt at 290°–292°, and sublime undecomposed when carefully heated. It is almost insoluble in ether, benzene, chloroform, and excess of caustic soda, difficultly soluble in glacial acetic acid and absolute alcohol, readily soluble in acetone. Gives with zinc-dust and KOH the anthraquinone reaction; reduction with zinc-dust and ammonia converts it into anthracene-2-carboxylic acid. Distillation over red-hot asbestos decomposes it into CO_2 and anthraquinone. It dissolves in sodium acetate and ammonium oxalate, and is not reprecipitated on the addition of acetic acid. Fusion with soda converts it into oxyanthraquinone carboxylic acid $C_{15}H_8O_5$.

The *Calcium salt* $Ca(C_{15}H_7O_4)_2$ and the *barium salt* $Ba(C_{15}H_7O_4)_2$ are sparingly soluble.

The *Ethyl ester* (Liebermann and Glock, Ber. 17, 890) $C_{15}H_7O_4{\cdot}C_2H_5$ is formed by the action of alcohol on the chloride. It crystallises in needles, melts at 147°, and is readily soluble in alcohol.

The *Chloride* $C_{15}H_7O_3Cl$ is produced by treating the acid with PCl_5. It crystallises from benzene in needles which melt at 147°.

The *Amide* $C_{14}H_7O_2CONH_2$ is obtained by passing NH_3 into a benzene solution of the chloride. It crystallises from a mixture of glacial acetic acid and benzene in needles, which melt at 280°, and are difficultly soluble in alcohol and benzene.

The *Anilide* crystallises from xylene in needles, m.p. 258°–260°.

Nitroanthraquinone carboxylic acid

$$C_{14}H_6(NO_2)O_2{\cdot}COOH$$

is produced by mixing the solution of the acid in concentrated sulphuric acid with nitric acid. Crystallises from glacial acetic acid in small needles, which melt above 300°. Gives with sulphuric acid a violet colouring matter.

1-*Nitroanthraquinone-2-carboxylic acid.* Terres (Ber. 1913, 46, 1638) prepared this derivative by oxidising 1-nitro-2-methylanthraquinone with chromic acid in concentrated nitric acid solution. It crystallises from acetic acid and melts at 283°. The corresponding amide occurs in nearly colourless prisms, m.p. 299°–301°. Further details of the preparation are given in D. R. P. 229394.

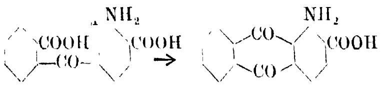
Dinitroanthraquinone-2-carboxylic acid (Limpricht, Annalen, 309, 122) is obtained by the oxidation of the corresponding anthranol with chromic acid in acetic acid solution. It forms yellow needles from alcohol and melts at 315°.

1-*Chloroanthraquinone-2-carboxylic acid.* This acid is an important intermediate in the manufacture of certain valuable vat-dyestuffs, especially Indanthrene Red BN. It may be prepared by oxidation of 1-chloro-2-methylanthraquinone by means of sodium dichromate in 90 p.c. acetic acid (Ullmann and Bincer, Ber. 1916, 49, 732) or alternatively by oxidation of the same substance with nitrous fumes in trichlorobenzene solution at 160° (D. R. P. 250742). It is also said to be obtained by the action of chlorine on a hot nitrobenzene solution of 1-nitro-2-methylanthraquinone. The acid crystallises in pale yellow needles, melting at 272°, and its methyl ester occurs as pale yellow leaflets, melting at 161·5°. The benzyl ester is prepared by the action of benzyl chloride and pyridine at 100° on the acid. This derivative crystallises from alcohol in yellow needles, melting at 135°–136°.

3-*Chloroanthraquinone-2 carboxylic acid* (Ullmann and Dasgupta, Ber. 1914, 47, 561) is obtained by the oxidation of the corresponding aldehyde, itself produced by the hydrolysis of 3-chloro-ω-dibromo-2-methylanthraquinone. The acid melts at 276°–278°, and its ethyl ester at 150°–151°.

5 : 8-*Dichloroanthraquinone-2-carboxylic acid* is produced in good yield by the chlorination of 'silver salt' dissolved in concentrated sulphuric acid at 125° and in presence of iodine. The substance is obtained in bright yellow crystals and melts above 300° (D. R. P. 255121). The constitution assigned to this substance is rendered probable by the preparation of derivatives, which show that the chlorine atoms are in the *p*-position to each other, and by the preparation of the isomeric 1 : 4-*dichloroanthraquinone-2-carboxylic acid* by oxidation of 1 : 4-dichloro-2-methylanthraquinone. This isomeric dichloro-acid melts at 246°–248° (D. R. P. 250742).

1-*Aminoanthraquinone-2 carboxylic acid.* This substance separates from nitrobenzene in brownish-red glistening needles, melting at 286°, and is prepared by the reduction of the corresponding nitro-compound by means of sodium sulphide (Terres, Ber. 1913, 46, 1637). It is also the product of the action of ammonia in presence of copper compounds on 1-chloroanthraquinone-2-carboxylic acid at elevated temperatures (D. R. P. 247411), and it may be synthesised by the action of 10 p.c. oleum on *o*-aminocarboxybenzoylbenzoic acid at 180° (D. R. P. 248838)



The amide melts at 279°–281°, and in addition, N-methyl, N-phenyl, N-*p*-chlorophenyl and N-β-naphthyl and similar derivatives have been described (D. R. P. 247411). Apparently the aminoanthraquinone-β-carboxylic acid described by Eckert (Monatsh. 1916, 35, 295) is a different substance. This melts at 338°, and is obtained by the reduction of the nitration product of anthraquinone-2-carboxylic acid.

3-*Aminoanthraquinone-2-carboxylic acid.* Willgerodt and Maffezzoli (J. pr. Chem. 1910, [ii.] 82, 210) obtained this acid by the action of hypochlorites on the half amide of anthraquinone-2 : 3-dicarboxylic acid. Another method is that of Ullmann and Dasgupta (Ber. 1914, 47, 562), who heated 3-chloroanthraquinone-2-carboxylic acid with aqueous ammonia and copper bronze at 160°–180° in an autoclave. The substance crystallises from nitrobenzene in brownish-yellow needles, melting at 362°–363° (U., D.), and forms an acetyl derivative, melting at 248° (W., M.). By replacing the ammonia in the above process by aromatic amines Ullmann and Dasgupta prepared N-aryl-derivatives such as 3-anilidoanthraquinone-2-carboxylic acid, m.p. 316°–317°, and 3-β-naphthylaminoanthraquinone-2-carboxylic acid, melting at 332°.

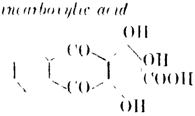
1 : 4-*Diaminoanthraquinone-2-carboxylic acid.* 2-Amino-5-acetylamino-4-carboxybenzoylbenzoic acid is heated with six times its weight of 95 p.c. sulphuric acid at 190°. The acid separates from alcohol in dark blue needles with bronze lustre, and melts above 350° (D. R. P. 261885).

A *Methoxyanthraquinone-β-carboxylic acid* is the product of the action of methylalcoholic sodium hydroxide on nitroanthraquinone-2-carboxylic acid (from the nitration of the acid). It crystallises in yellow needles, melting at 279° (Eckert, Monatsh. 1914, 35, 284).

3-*Phenoxyanthraquinone-2-carboxylic acid* is prepared by heating 3-chloroanthraquinone-2-carboxylic acid with phenol, potassium carbonate and copper bronze (Ullmann and Dasgupta, *l.c.*). The nearly colourless needles melt at 270°.

Quinizarine-β-carboxylic acid. β-Methylquinizarine is oxidised by gradually heating to 150° with 90 p.c. sulphuric acid, sodium nitrite and boric acid. The acid crystallises from nitrobenzene in yellow-brown needles melting at 244°–246° (D. R. P. 273341)

Purpurincarboxylic acid



This compound is prepared from alizarine carboxylic acid by oxidation with manganese dioxide in sulphuric acid solution (D. R. P. 260765, 272301). It is a red powder, but may be crystallised from chloroform in glistening red leaflets melting at 222°–224°.

Under the heading methylanthracene, besides *o*- and *m*-methylanthracene two other substances are to be found in chemical literature.

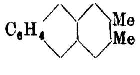
*iso***Methylanthracene** (Bornstein, Ber. 15, 1821) obtained by digesting *iso*methylanthraquinone with zinc-dust and ammonia, and by distilling *p*-toluene phthaloylic acid (Gresly, Annalen, 234, 238), with zinc-dust, is evidently identical with β-methylanthracene.

Methanthrane $C_{15}H_{12}$ (Oudemans, J. pr. Chem. [ii.] 9, 416), obtained by distilling podocarpinic acid $C_{17}H_{22}O_3$ with zinc-dust, is probably not an anthracene derivative at all. It melts at 117°, and gives on oxidation with CrO_3 and acetic acid, methanthraquinone $C_{15}H_{10}O_2$ which crystallises from 70 p.c. alcohol in orange-red needles melting at 187°.

It therefore possesses more the properties of a phenanthrene than of an anthracene derivative.

DIMETHYLANTHRACENES.

***o*-Dimethylanthracene**

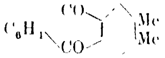


(Elbs, J. pr. Chem. 1890, 41, 5) is readily prepared by the reduction of the corresponding (2, 3) dimethylanthraquinone with zinc-dust and ammonia.

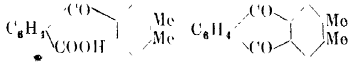
5 grams of the quinone, 30 grams zinc-dust, and 500 c.c. aqueous ammonia (equal parts of concentrated ammonia solution and water), are heated to boiling until the red liquid which is produced at first has become colourless. The mass is then filtered, the residue washed with hot water, dried in a water oven, and repeatedly extracted with boiling alcohol. The clear alcoholic extract deposits on cooling yellowish plates of dimethylanthracene. *o*-Dimethylanthracene melts at 246°, and sublimes in colourless plates which possess a bluish-green fluorescence. It is readily soluble in benzene and hot alcohol, but difficultly soluble in cold alcohol.

The picric acid compound crystallises in long garnet-red needles; it is readily decomposed by alcohol.

o- or (2, 3) **Dimethylanthraquinone**

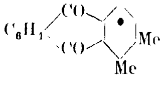


is obtained synthetically by heating *o*-xyloyl-*o*-benzoic acid with H_2SO_4.



1 part of *o*-xyloyl-*o*-benzoic acid is dissolved in 6 parts of warm concentrated H_2SO_4, and the mixture heated at 128° for a quarter to half an hour, the dark-coloured solution poured into a dish, and placed next to a dish of water. As the solution becomes dilute the quinone crystallises out, the operation being complete in 3-4 days.

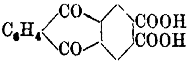
The precipitate is collected, washed with water and dilute ammonia, and purified either by sublimation or recrystallisation from xylene; *o*-dimethylanthraquinone is thus obtained in long yellow needles which melt at 183°. It is readily soluble in hot xylene, benzene, and alcohol, and is readily reduced by zinc-dust and ammonia to *o*-dimethylanthracene, hence its constitution is probably that given above, and not



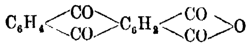
(Compare action of zinc-dust and ammonia on dimethylanthraquinones with a CH_3 group in the 1 or 4 position.)

A dimethyl anthraquinone, which is probably identical with this, is obtained by oxidising dimethyl anthranol with chromic acid in acetic acid solution (Limpricht and Mārtens, Annalen, 312, 103). It forms yellow needles from alcohol and melts at 200°.

Anthraquinone-2 : 3-dicarboxylic acid



is produced by heating *o*-dimethylanthraquinone (3 grams) with 20–25 c.c. of nitric acid (sp.gr. 1·1) in a sealed tube at 210°–220° for five hours. It crystallises in yellow needles, melts at 340°, and when strongly heated sublimes in yellow plates, which melt at 290°, and consist now of anthraquinone dicarboxylic anhydride.



$$C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{CO}_{CO}{>}O$$

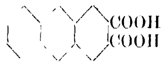
Ammonium salt. Red amorphous mass, easily soluble in water.

Calcium salt. Light red precipitate, almost insoluble in water.

Lead salt. Light red precipitate, almost insoluble in water.

Silver salt. Light red precipitate; is decomposed on heating into CO_2, Ag, and anthraquinone.

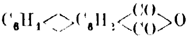
Anthracene-2 : 3-dicarboxylic acid



is readily prepared by treating the solution of the ammonium salt of anthraquinone dicarboxylic acid with zinc-dust and ammonia until the red solution becomes yellowish-green coloured; and then precipitating the clear solution with HCl.

Anthracene-*o*-dicarboxylic acid crystallises from alcohol in small yellowish-green crystals, which melt at 345°. It is insoluble in water, readily soluble in alcohol. The solution in dilute ammonia fluoresces blue-green, that in dilute NaOH blue.

The acid, if carefully heated, gives a yellowish-red sublimate of anthracene-*o*-dicarboxylic anhydride



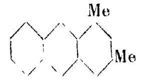
$$C_6H_4{<}{>}C_6H_2{<}^{CO}_{CO}{>}O$$

Calcium salt. Brownish-green precipitate, almost insoluble in water.

Lead salt. Yellowish precipitate, insoluble in water.

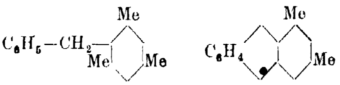
Silver salt Yellowish-brown precipitate, insoluble in water; decomposes on distillation into CO_2, Ag, and anthracene.

m-**Dimethylanthracene**

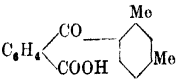


(Elbs, J. pr. Chem. 1890, 41, 13). This hydrocarbon cannot be produced by the reduction of *m*-methylanthraquinone with zinc-dust and ammonia.

It is obtained by passing mesitylphenyl methane (Louise, Ann. Chim. [vi.] 5, 187, 193) through a red-hot tube



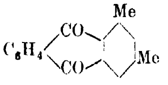
Or by distilling *m*-xyloyl-*o*-benzoic acid



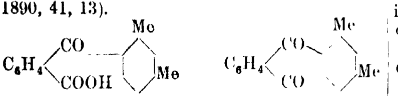
with zinc-dust (Gresly, Annalen, 234, 238).

m-Dimethylanthracene crystallises from alcohol in colourless plates, which melt at 202°–203°. Gives with bromine γ-brom-*m*-dimethyl anthracene tetrabromide (m.p. 175°–180°).

m-**Dimethylanthraquinone**

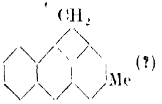


is prepared by the action of sulphuric acid on *m*-xyloyl-*o*-benzoic acid (Elbs, J. pr. Chem. 1890, 41, 13).



1 part of the pure acid is dissolved in 7–10 parts of concentrated sulphuric acid, the clear solution heated at 110°–125° for half an hour, the product poured in a thin stream into water, and the precipitate treated as described under *m*-methylanthraquinone. Yield 60–70 p.c. of theory. *m*-Dimethylanthraquinone crystallises in small needles which melt at 162°. It dissolves with difficulty in alcohol and benzene. Zinc-dust and ammonia reduces it to *m*-dimethylanthracylene $C_{16}H_{12}$, and not to dimethylanthracene.

m-**Dimethylanthracylene**



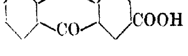
Preparation.—*m*-Dimethylanthraquinone (5 grams), finely powdered, is mixed with zinc-dust (30 grams) and concentrated aqueous ammonia (200 c.c.), and a solution (5 c.c.) of basic copper carbonate in ammonia added. The product is well agitated, and gently warmed until it has assumed a light green colour, then boiled for six hours with the addition from time to time of small quantities of copper carbonate dissolved in ammonia. The mass is filtered, the precipitate washed with water, dried at the ordinary temperature, and extracted with boiling alcohol. The alcoholic solution on cooling deposits a small quantity of crystals, which are filtered off. The mother liquor is partially evaporated, again allowed to stand, filtered from the crystals which form, and this operation repeated until oily drops appear. The remainder of the hydrocarbon present in the mother liquor is purified by conversion into the picric acid compound and decomposing this with ammonia or sodium hydroxide solution (Elbs, *l.c.*).

m-Dimethylanthracylene crystallises from alcohol in groups of colourless plates which melt at 85°. It is readily soluble in hot alcohol and glacial acetic acid, difficultly soluble in cold alcohol.

With picric acid it forms a deep garnet-red compound $C_{16}H_{12}$-$C_2H_2(NO_2)_3OH$, which is not decomposed by alcohol. M.p. 135°.

Treated with bromine in CS_2 solution (4 at. Br. to 1 mol. $C_{16}H_{12}$) an unstable dibromo compound $C_{16}H_{10}Br_2$ is produced, which crystallises from CS_2 in sulphur-yellow prisms, which melt at 175° with decomposition.

Anthraquinone-*m*-dicarboxylic acid



This acid is produced quantitatively by the oxidation of *m*-dimethylanthraquinone with dilute nitric acid (for details, *v.* the *o-dicarboxylic acid*) or by the oxidation of 3-methylanthraquinone-1-carboxylic acid by means of permanganate (D. R. P., 259365, 1913). It crystallises in fine yellow needles, which sublime above 230° without melting. It is almost insoluble in water, and difficultly soluble in the ordinary organic solvents.

Ammonium salt. Reddish warty masses, easily soluble in water.

Potassium salt. Reddish gelatinous mass, which becomes crystalline on standing, and contains then 2 mol. of water of crystallisation.

Sodium salt. Reddish crystalline crusts, contains 9 mol. of water of crystallisation.

Calcium salt. Light red powder, insoluble in water and alcohol.

Barium salt. Light violet powder, contains 1 mol. of water of crystallisation.

Lead salt. Red powdery precipitate, insoluble in water and alcohol.

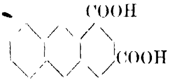
Copper salt. Dark green crystalline powder, contains 1 mol. of water of crystallisation, insoluble in water and alcohol.

Silver salt. Pinkish precipitate, almost insoluble in water and alcohol. Decomposes on heating into CO_2, Ag, and anthraquinone.

Anthraquinone-*m*-dicarboxyl chloride is obtained by warming the acid (5 grams) with phosphorus pentachloride (7·5 grams), distilling off the phosphorus oxychloride at 140°, and shaking the residue with water and chloroform The chloroform solution is dried over $CaCl_2$ and evaporated, when the acid chloride remains behind as a reddish mass, which showed little tendency to crystallise.

The *acid amide* prepared by treating the chloride with ammonia is also difficult to obtain in a crystalline condition.

Anthracene-*m*-dicarboxylic acid



is prepared by reducing anthraquinone-*m*-dicarboxylic acid with zinc-dust and ammonia (for details, *v.* the *o*-dicarboxylic acid). Crystallises in brownish-yellow masses, which do not melt at 330°. It is almost insoluble in water, difficultly soluble in most other solvents.

Ammonium salt. Greyish-green crystalline powder, readily soluble in water, difficultly soluble in dilute alcohol.

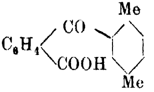
Copper salt. Dirty-green precipitate, almost insoluble in water and alcohol. Dissolves in ammonia, producing a yellow solution with a strong blue fluorescence (characteristic).

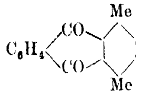
Silver salt. Light brown powder. Dissolves in ammonia, producing a yellow solution with a blue fluorescence.

The chloride of the acid has the same properties and is produced in the same manner as the chloride of anthraquinone-*m*-dicarboxylic acid

p-**Dimethylanthraquinone**

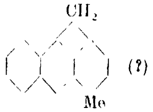
is produced by the action of H_2SO_4 on *p*-xyloyl-*o*-benzoic acid, at a temperature of 125° (Elbs, J. pr. Chem. 1890, 41, 27; Gresly, Annalen, 234, 240).





The details of the preparation and purification are the same as those of the ortho derivative. Yield 50–65 p.c. of the theoretical. *p*-Dimethylanthraquinone crystallises from xylene in yellow needles, which melt at 118°–119°. It is readily soluble in benzene and xylene, sparingly soluble in alcohol.

***p*-Dimethylanthracylene**

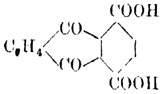


is produced when *p*-dimethylanthraquinone is reduced with zinc-dust and ammonia (*v.* *m*-dimethylanthracylene).

It crystallises from alcohol in plates which melt at 63°.

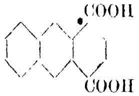
The picrate $C_{16}H_{12}, C_6H_2(NO_2)_3OH$ crystallises from alcohol in dark red needles, which melt at 129°.

Anthraquinone-*p*-dicarboxylic acid



is prepared by oxidising *p*-dimethylanthraquinone with dilute nitric acid (for details, *v.* the *o*- and *m*- derivatives). Yield nearly quantitative. It crystallises in small yellow crystals, which are difficultly soluble in water, but readily soluble in alcohol. The melting-point lies above 300°. The salts are similar to those of the *o*- and *m*- derivatives.

Anthracene-*p*-dicarboxylic acid

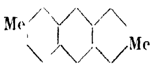


is obtained in the same way as its isomerides, by reducing anthraquinone *p*-dicarboxylic acid with zinc-dust and ammonia.

It crystallises from alcohol in the form of a light brown crystalline powder which melts at about 320°. It is readily soluble in alcohol, but almost insoluble in water.

The salts are similar to those of the *o*-acid.

2 : 6-**Dimethylanthracene**



Friedel and Crafts (Ann. Chim. [vi.] 11, 265) obtained an unseparated mixture of dimethylanthracenes and other substances by each of two reactions, namely by the action of aluminium chloride on toluene and methylene chloride, or on toluene and acetylene tetrabromide.

Lavaux (Compt. rend. 139, 976) isolated from this product, benzene, xylene, dimetatolylmethane, diparatolylmethane, β-methylanthracene, and three isomeric dimethylanthracenes, having m.ps. 240°, 244·5°, and 86° respectively. The substance of m.p. 244·5° is 2 : 6-dimethylanthracene and the constitution is proved by the following synthesis taken in conjunction with the other evidence:

m-Tolyl *m*-4 xylylketone (Seer, Monatsh. 32, 143) from *m*-toluoyl chloride and *m*-xylene, when boiled for five days is changed to 2 : 6-dimethylanthracene of m.p. 243°.

The hydrocarbon can also be prepared (Anschütz, Annalen, 235, 319) by distilling the tetrahydride of the tetramethylanthracene of Anschutz with zinc-dust. This preparation harmonises better with the constitution 2 : 4 : 6 : 8 for the latter hydrocarbon than for the 1 : 3 : 6 : 8 structure assigned by Dewar and Jones (*v. infra*).

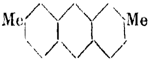
The substance crystallises from benzene in greenish-yellow plates and is readily soluble in benzene, difficultly so in alcohol.

2 : 6-**Dimethlyanthraquinone** is produced by the oxidation of the anthracene derivative by chromic acid in acetic acid solution. It is also obtained in 19 p.c. yield by heating *m*-toluoyl chloride and aluminium chloride at 130° for two hours and then at 130°–140° for 16 hours. It is very sparingly soluble and crystallises from acetic acid, nitrobenzene, or in the form of long silky needles from alcohol. It melts at 236°.

Anthraquinone,2 : 6-**dicarboxylic acid** is obtained when the above quinone is boiled with chromic acid and acetic acid for 60 hours. It forms a chloride which has m.p. 197°–198°, and this with alcoholic ammonia yields an amide $C_{16}H_{10}O_4N_2$, infusible at 370°.

2 : 6-**Di-α-naphthoylanthraquinone** $C_{36}H_{20}O_4$, m.p. 183°–185°, is obtained from the chloride, naphthalene, and aluminium chloride in nitrobenzene at 75°–80° after 20 hours.

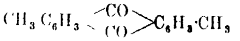
2 : 7-**Dimethylanthracene** (α and γ-dimethylanthracenes)



This hydrocarbon is produced (Elbs and Wittich, Ber. 18, 348) when a mixture of 3 parts toluene, 3 parts carbon disulphide, and 1 part chloroform is treated with 2 parts of aluminium chloride. It is formed further (1) together with ditolylmethane $C_{15}H_{16}$ and *m*- and *p*-xylene, by treating a mixture of toluene and methylene chloride with aluminium chloride (Friedel and Crafts, Bull. Soc. chim. [ii.] 41, 323); (2) by treating xylyl chloride $CH_3{\cdot}C_6H_4{\cdot}CH_2Cl$ with aluminium chloride (Friedel and Crafts, *ibid.* [ii.] 41, 326); (3) by treating toluene and acetylene tetrabromide with aluminium chloride (Anschütz and Immendorff, Ber. 17, 2816; Annalen, 235, 172); (4) by treating toluene with nickel carbonyl and aluminium chloride. In this reaction, *p*-tolualdehyde is a by-product (Dewar and Jones, Chem. Soc. Trans. 85, 212).

It is identical with the hydrocarbon isolated by Zincke and Wackendorff (Ber. 10, 1481) from the higher boiling fractions of coal tar. It crystallises from alcohol in glittering yellowish plates which melt at 215° (Elbs, *l.c.*; Dewar and Jones, *l.c.*); 224°–225° (Friedel and Crafts, *l.c.*). It sublimes readily, is moderately soluble, and yields the following oxidation products.

γ-Dimethylanthraquinone (Zincke and Wackendorff, *l.c.*).

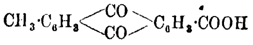


$$\mathrm{CH_3\,C_6H_3}<\substack{\mathrm{CO}\\ \mathrm{CO}}>\mathrm{C_6H_3{\cdot}CH_3}$$

is produced by the oxidation of the above hydrocarbon with CrO_3 and acetic acid; it crystallises from dilute alcohol in small straw-yellow needles, which melt at 155°.

It sublimes in almost colourless flat needles, is moderately soluble in alcohol, ether, benzene, glacial acetic acid, and hot light petroleum.

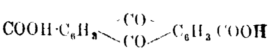
Methylanthraquinone carboxylic acid



$$\mathrm{CH_3{\cdot}C_6H_3}<\substack{\mathrm{CO}\\ \mathrm{CO}}>\mathrm{C_6H_3{\cdot}COOH}$$

is produced by the oxidation of γ-dimethylanthracene (m.p. 224°–225°) with CrO_3 and acetic acid. It crystallises in flocks, which melt at 244°–246°, and sublime, when strongly heated, in small needles.

Anthraquinone dicarboxylic acid



$$\mathrm{COOH{\cdot}C_6H_3}<\substack{\mathrm{CO}\\ \mathrm{CO}}>\mathrm{C_6H_3\,COOH}$$

is formed, together with dimethylanthraquinone and methylanthraquinone carboxylic acid, by oxidising γ-dimethylanthracene with CrO_3. It crystallises in small warty masses (m.p. not given). It is readily separated from methylanthraquinone carboxylic acid by treatment with concentrated NaOH, in which the sodium salt of the dicarboxylic acid is readily soluble, but that of the monocarboxylic acid sparingly soluble. The solution of the acid in KOH becomes violet on exposure to the air. The Ba and Ca salts are gelatinous and insoluble.

DIMETHYL ANTHRACENE DERIVATIVES.

Nitro - compounds. 4-*Nitro*-1 : 3-*dimethylanthraquinone* of m.p. 234° is obtained by boiling 1 : 3-dimethylanthraquinone with nitric acid (sp.gr. 1·37) for 10 hours. It is reduced by alkaline hyposulphite to the *amino* compound which has practically the same m.p. 4-*Iodo*-1 : 3 - *dimethylanthraquinone*, m.p. 118°, is produced when the diazotised amine is treated with potassium iodide (Scholl and Potschiwauscheg, Ber. 43, 346). 2 : 4 - *Dinitro* - 1 : 3 - *dimethyl* - *anthraquinone* melts at 283°–285°, and is produced by agitating the quinone for many hours with fuming nitric acid (sp.gr. 1·52).

1 : 5 - *Dinitro* - 2 : 6 - *dimethylanthraquinone* (?) (Seer, *l.c.*) is obtained by the nitration of 2 : 6 - dimethylanthraquinone with sulphuric acid and potassium nitrate. It forms colourless needles and on reduction with alkaline hyposulphite yields the corresponding *diamine*, dark red needles, melting at 255°–256°. The corresponding *diiodo* compound, obtained in the usual way, forms orange-yellow needles, m.p. 273°.

1-*Amino*-2 : 4-*dimethylanthraquinone* separates from benzene in dark red crystals melting at 293°. It is prepared by ring closure of 5′-amino-2-*m*-xyloylbenzoic acid with 90 p.c. sulphuric acid (D. R. P. 234917).

Chloro-derivatives (Harrop, Norris and Weizmann, Chem. Soc. Trans. 95, 1312).

3 : 6-Dichlorophthalic anhydride was condensed with the three xylenes by means of aluminium chloride in carbon disulphide solution.

The benzoylbenzoic acids were converted to the corresponding quinones by heating with sulphuric acid containing boric acid and 10 p.c. of sulphur trioxide for 10 minutes at 120°.

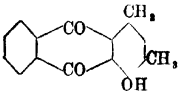
5 : 8 - *Dichloro* - 1 : 2 - *dimethylanthraquinone* from *o*-xylene crystallises from acetic acid in greenish-yellow needles and melts at 269°–270°. Its colour in sulphuric acid is orange-red.

5 : 8 - *Dichloro* - 1 : 3 - *dimethylanthraquinone* is produced in poor yield. It crystallises from xylene in light yellow needles and melts at 208°.

5 : 8 - *Dichloro* - 1 : 4 - *dimethylanthraquinone* melts at 244°. When these chloro compounds are heated with aniline, sodium phenoxide, or phenyl mercaptan and caustic soda, the chlorine atoms are replaced by the groups —NHPh, —OPh, and —SPh respectively.

Hydroxy derivatives.

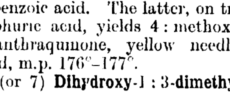
4-Hydroxy - 1 : 3 - dimethylanthraquinone (Bentley, Gardner and Weizmann, *l.c.*)



Phthalic anhydride and *m*-4-xylenol, when fused together with boric acid, yield a benzoyl benzoic acid which, on further treatment with sulphuric acid, changes to this quinone. It crystallises in needles from acetic acid and melts at 173°–175°.

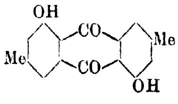
Methyl ether. Phthalic anhydride and *m*-4 : xylyl methyl ether in presence of aluminium chloride yield 2′-methoxy -3′ : 5′-dimethyl - 2 - benzoyl benzoic acid. The latter, on treatment with sulphuric acid, yields 4 : methoxy : 1 : 3 : dimethylanthraquinone, yellow needles from acetic acid, m.p. 176°–177°.

4 : 6- (or 7) **Dihydroxy-1 : 3-dimethylanthraquinone.**

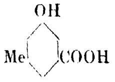


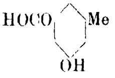
This quinone is obtained direct by the condensation of 4-hydroxyphthalic anhydride with *m* - 4 - xylenol by means of boric acid. It crystallises in yellow needles from acetic acid and melts at 270°. Its solution in sulphuric acid is intensely bluish-red (Bentley, Gardner and Weizmann, *l.c.*).

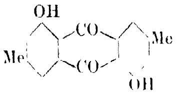
Dimethylanthrarufin (Kostanecki and Niementowski, Ber. 18, 250)



is obtained, together with small quantities of two other isomers, by heating symmetrical *m*-hydroxytoluic acid with sulphuric acid.







The crude product is poured into water, the precipitate collected, washed with water, and treated with baryta water, which leaves the dimethylanthrarufin undissolved. The baryta extract is precipitated with HCl, the precipitate extracted with alcohol. Dimethylbenzdihydroxyanthraquinone dissolves, whereas dimethylanthraflavic acid is insoluble (*v. infra*).

Dimethylanthrarufin crystallises from benzene in yellow silky needles, which melt at 300° and sublime in orange-red needles. It does not dye mordanted cloth. The solution in sulphuric acid is cherry-red coloured, and similar to that of anthrarufin in H_2SO_4. The *diacetate*

$$C_{16}H_{10}O_2(C_2H_3O_2)_2$$

crystallises in yellow plates, m.p. 236°-237°.

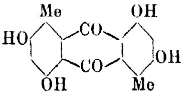
Dimethylanthraflavic acid (for preparation, *v. Dimethylanthrarufin*). It sublimes in yellow needles which do not melt at 360°. It is insoluble in benzene, difficultly soluble in alcohol and glacial acetic acid; it dissolves in alkalis and sulphuric acid with a yellow colour like anthraflavic acid. It does not dye mordanted cloth. The *diacetate* crystallises in needles which melt at 223°.

Dimethylbenzdihydroxyanthraquinone (for preparation, *v. Dimethylanthrarufin*). It crystallises from alcohol in yellow needles which melt at 213°. It dissolves in glacial acetic acid, but is sparingly soluble in alcohol and benzene. It does not dye mordanted cloth. The *diacetate* melts at 188°.

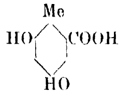
1 : 5 - **Dihydroxy**-2 : 6 - **dimethylanthraquinone** and 3 : 7-**dihydroxy**-2 : 6-**dimethylanthraquinone** are together obtained by the action of concentrated sulphuric acid on 2 hydroxy-*p*-toluic acid (Me=1). The former crystallises in scarlet crystals from chloroform and petroleum ether and melts at 224°-225° whilst the latter separates from alcohol in acicular crystals melting at 232°.

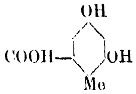
3 : 5-**Dihydroxy**-2 : 6-**dimethylanthraquinone** is similarly obtained from 3-hydroxy-*p*-toluic acid. It occurs in bright golden-yellow leaflets melting at over 300° and yields an *acetyl*-derivative melting at 215°, a *diacetyl*-derivative melting at 196° and a *monomethyl ether* melting at 214°-215° (Jowett and Potter, T., 1903, 83, 1331).

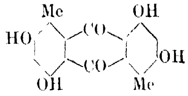
Dimethylanthrachrysone (Cahn, Annalen, 240, 280)



is prepared by heating cresorsellinic acid (1 part) with concentrated sulphuric acid (10 parts) to 100°.



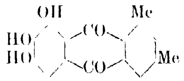




It crystallises from alcohol in bronze-coloured needles which do not melt when heated to 360°. It sublimes with difficulty, and then with considerable decomposition. It is insoluble in water, benzene, and light petroleum, sparingly soluble in alcohol and CS_2, readily soluble in $CHCl_3$, acetone, and glacial acetic acid. It is soluble in solutions of the alkalis and alkaline earths, with a yellowish-red colour. The solution in sulphuric acid is magenta-coloured, and shows two absorption bands in the green. It does not dye mordanted cloth.

The *tetraacetyl derivative* $C_{16}H_8O_2(C_2H_3O_2)_4$ crystallises in yellowish needles which melt at 234° and are readily soluble in hot alcohol, glacial acetic acid, and benzene.

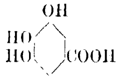
Dimethylanthragallol (Birukoff, Annalen, 240, 287).

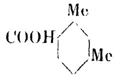


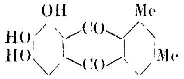
is obtained by heating a mixture of 5 parts xylylic acid

$$C_6H_3(COOH)(CH_3)(CH_3),(COOH:CH_3:CH_3=1, 2, 4)$$

with 3 parts of gallic acid and 40 parts H_2SO_4.





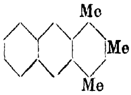


The product is mixed with water, the precipitate collected, washed with water, dissolved in absolute alcohol (in which small quantities of accompanying rufigallic acid are insoluble); evaporated and the residue extracted with benzene; again evaporated, and the product recrystallised from acetone. Glittering reddish-yellow needles (no m.p. given). Distilled with zinc-dust, dimethylanthracene (m.p. 224°) results. The absorption spectrum of a solution of dimethylanthragallol in concentrated sulphuric acid is almost identical with that of anthragallol itself.

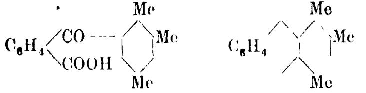
This substance should, from its method of preparation, be a derivative of *m*-dimethylanthracene, which, however, melts at 202°-203°, whereas the dimethylanthracene obtained from dimethylanthragallol melts at 224°, and is evidently identical with that obtained from coal tar by Zincke and Wackendorff. This point requires investigation.

Trimethylanthracenes (Elbs, J. pr. Chem. 1890, 41, 121).

(1, 2, 4) **Trimethylanthracene**



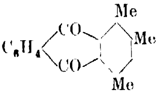
is produced by the distillation of pseudocumoyl-*o*-benzoic acid with zinc-dust (Gresly, Annalen, **234, 241**).



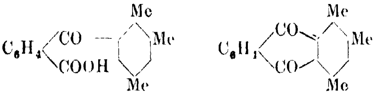
Preparation.—5 grams of the powdered acid are intimately mixed with 10 grams of zinc-dust, and distilled from a retort, the temperature being raised very gradually. The greenish-coloured oil which first passes over is separated from the reddish-coloured oil, which distils last and crystallises on cooling; the latter is dissolved in boiling light petroleum, and the crystals which separate out on cooling purified by re-crystallisation.

Trimethylanthracene crystallises in white plates, possessing a blue fluorescence, and which melt at 244°. The picrate crystallises from benzene in brownish-red needles, which melt at 145° and are decomposed by alcohol.

(1, 2, 4) **Trimethylanthraquinone**



is obtained by the action of dehydrating agents on pseudocumoyl-*o*-benzoic acid.



In order to obtain a good yield of this substance, the following directions must be carefully observed.

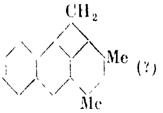
10 grams of powdered *pseudo*cumoyl-*o*-benzoic acid are dissolved in 100 c.c. of concentrated sulphuric acid, and the product gently warmed. The solution, which becomes clear and cherry-reddish coloured at 60°, is heated at 115° for one hour, allowed to cool to 70°-80°, and then mixed with 10 grams of phosphorus pentoxide, the temperature being allowed to rise gradually to 115°-120° during the addition, at which temperature it is kept for further two hours. The well-cooled product is poured in a thin stream into water, the precipitate collected, washed with water, and then with cold carbonate of soda solution; dried at 100°, and recrystallised from a mixture of alcohol and xylene. Trimethylanthraquinone crystallises in long yellow needles which sublime readily and melt at 162°-163°. It is readily soluble in ether, benzene, and xylene; sparingly soluble in alcohol.

α-*Nitro*-1 : 2 : 4-*trimethylanthraquinone*, melting at 195°-200°, is the product of nitration of trimethylanthraquinone with a limited amount of potassium nitrate in sulphuric acid solution, whilst the β-nitro-derivative results from nitration with concentrated nitric acid at 0° (Elbs, J. pr. Ch., 1890, [ii.] 41, 134).

β-*Amino*-1 : 2 : 4-*trimethylanthraquinone* crystallises from dilute alcohol in dark red needles and melts at 154°-155°.

5 : 6 : 7 - *Trihydroxy*-1 : 2 : 4 - *trimethylanthraquinone* has been prepared by Wende (Annalen, 1887, 240, 290), by condensing duric acid (from ψ-cumidine) with gallic acid. The substance crystallises from dilute alcohol in brown needles, and melts at 244°. The absorption spectrum resembles that of anthragallol. The triacetate melts at 174°.

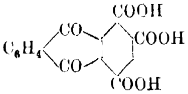
(1, 2, 4) **Trimethylanthracylene**



results from the action of zinc-dust and ammonia on trimethylanthraquinone (for details, *v.* dimethylanthracylene). It crystallises from alcohol in colourless plates which melt at 64° and resemble naphthalene in appearance. The picrate $C_{17}H_{14}{\cdot}C_6H_2(NO_2)_3OH$ melts at 134°, and is decomposed by alcohol.

Bromine converts the hydrocarbon into the unstable dibromo-trimethylanthracylene.

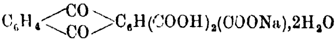
Anthraquinone-1 : 2 : 4-**Tricarboxylic acid**



is produced by the oxidation of (1, 2, 4) trimethylanthraquinone with dilute nitric acid (*v. Anthraquinone dicarboxylic acids*). It crystallises from alcohol in yellowish-white warty masses, which do not melt at 320°; It is almost insoluble in water.

The *ammonium* salt separates from its solution in reddish amorphous crusts, which dissolve in water with a deep red colour.

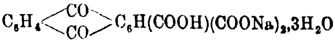
The *primary sodium salt*



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H(COOH)_2(COONa),2H_2O$$

crystallises in yellow plates, readily soluble in hot, but difficultly in cold water.

Secondary sodium salt



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H(COOH)(COONa)_2,3H_2O$$

crystallises in yellowish-red plates, more soluble in water than the primary salt.

Tertiary sodium salt is very readily soluble in water, and difficult to obtain in a crystalline form.

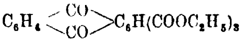
Neutral calcium salt. Rose-red plates from water.

Neutral copper salt. Light green precipitate, very difficultly soluble in water.

Neutral lead salt. Yellow powdery precipitate insoluble in water.

Neutral silver salt. Reddish powdery precipitate which, when heated to a high temperature, decomposes into CO$_2$, Ag, and anthraquinone.

The *triethyl ester*



$$C_6H_4<^{CO}_{CO}>C_6H(COOC_2H_5)_3$$

crystallises from alcohol in glittering white plates, which melt at 125°.

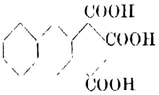
When treated with nitric acid and sulphuric acid trimethylanthraquinone yields three nitro-derivatives which, on oxidation, yield two mononitro- and one dinitro-anthraquinone tricarboxylic acids.

I. *Mononitro-anthraquinone* (1, 2, 4) *tricarboxylic acid*, $C_{12}H_4(CO)_2(COOH)_3(NO)_2$, crystallises in small yellow crystals which melt at 308°–310°. It is soluble in alcohol, ether, acetone, glacial acetic acid, and benzene, insoluble in water.

II. *Mononitroanthraquinone tricarboxylic acid* crystallises in small crystals, which melt at 360°–370° with decomposition, is readily soluble in alcohol, ether, and benzene, insoluble in water. The copper salts of these two acids differ very distinctly. That of acid I. crystallises in green needles, which dissolve in ammonia with a green colour; that of acid II. crystallises in red needles which dissolve in ammonia, forming a red solution.

Dinitro anthraquinone (1, 2, 4) *tricarboxylic acid*, $C_{12}H_3(NO_2)_2(CO)_2(COOH)_3$, melts at 340°–360° with decomposition.

Anthracene-1 : 2 : 4 tricarboxylic acid

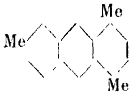


is readily obtained by reducing anthraquinone (1, 2, 4) tricarboxylic acid with zinc-dust and ammonia (for details, see the corresponding dicarboxylic acids). It is readily soluble in benzene and light petroleum, still more readily in alcohol, with a yellowish-green colour, insoluble in water. No sharp m.p. was observed, as the acid sublimed above 260°, being converted probably into the anhydride.

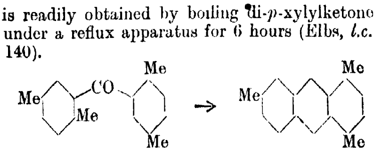
The *alkali salts* are very readily soluble in water, and do not crystallise readily.

The *silver salt* is a yellowish-green precipitate which, on heating, is decomposed, yielding a sublimate of anthracene.

(1, 4, 7) Trimethylanthracene



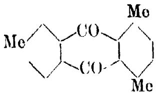
is readily obtained by boiling di-*p*-xylylketone under a reflux apparatus for 6 hours (Elbs, *l.c.* 140).



The yield is about 20–25 p.c. of the theoretical.

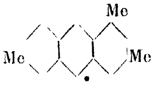
It crystallises in thin colourless plates, which fluoresce bluish-green, melt at 227°, and sublime with great readiness, even at 100°. It is difficultly soluble in cold alcohol, more readily soluble in hot alcohol, benzene, and ether.

(1, 4, 7) Trimethylanthraquinone

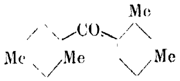


is obtained by oxidising (1, 4, 7) trimethylanthracene with the theoretical quantity of CrO_3 in glacial acetic acid solution. The yield is almost quantitative. It crystallises in yellow needles, which melt at 184°, and sublime with great readiness. It dissolves readily in glacial acetic acid, but is only sparingly soluble in alcohol. With zinc-dust and KOH it gives the anthraquinone reaction. On further oxidation this substance yields a mixture of carboxylic acids which could not be satisfactorily separated.

(1, 3, 6) Trimethylanthracene

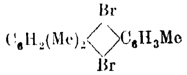


is synthetically prepared by the action of heat on di-*m*-xylylketone (Elbs, *l.c.* 142).



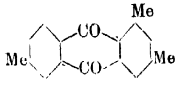
The yield is 20–25 p.c. of the theoretical. It crystallises from a mixture of alcohol and acetone in plates which melt at 222°, is difficultly soluble in alcohol and light petroleum, more readily in ether and glacial acetic acid, very readily in CS_2, acetone, and benzene.

γ-Dibromo (1, 3, 6) *trimethylanthracene*



results when trimethylanthracene (1 mol.) dissolved in CS_2 is treated with bromine (2 mol.). On evaporation a brownish-yellow crystalline mass is obtained, which crystallises from acetone in rosettes of yellow plates which melt at 142°.

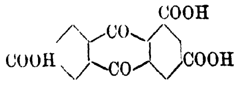
(1, 3, 6) Trimethylanthraquinone



is produced by oxidising (1, 3, 6) trimethylanthracene with the calculated quantity of chromic acid in acetic acid solution.

It crystallises in yellow needles which melt at 190°, are readily soluble in glacial acetic acid, difficultly soluble in alcohol. It sublimes readily and gives with zinc-dust and potash a deep red solution.

Anthraquinone (1, 3, 6) tricarboxylic acid



To prepare this substance 0·5 gram (1, 3, 6) trimethylanthracene is heated with 15 grams HNO_3 (sp.gr. 1·1) in a sealed tube 10 hours to 180°, then 10 hours to 210°-220°. The tricarboxylic acid crystallises out in yellow plates It is scarcely soluble in water, and very difficultly soluble in other solvents; it does not melt when heated to 300°.

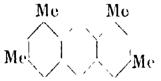
The *ammonium salt* is readily soluble in water, and crystallises in flesh-coloured plates.

The *barium salt* is a cherry-red crystalline precipitate, very sparingly soluble in water.

Tetramethylanthracene (Anschütz, Annalen, 235, 174) $C_{14}H_6(CH_3)_4$ is formed in small quantity, together with toluene and trimethylbenzene, by the action of aluminium chloride on a mixture of acetylenetetrabromide and *m*-xylene; m.p. 280°. If *o*-xylene be used in the place of *m*-xylene in the above reaction, a tetramethylanthracene, which melts above 280°, is obtained; in the case of *p*-xylene being used the tetramethylanthracene obtained melts at about 280°.

Since there are only two isomeric tetramethylanthracenes derivable from *m*-xylene, namely 1 : 3 : 6 : 8 and 2 : 4 : 6 : 8, and the former is chosen for the quinone described below, the hydrocarbon of Anschütz is probably 2 : 4 : 6 : 8-tetramethylanthracene.

1 : 3 : 6 : 8-**Tetramethylanthracene**

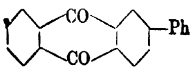


Dewar and Jones (Chem. Soc. Trans 1904, 85, 212) obtained this hydrocarbon by the action of nickel carbonyl on *m*-xylene in presence of aluminium chloride.

The hydrocarbon is purified by successive crystallisation from hot benzene and acetic acid. It forms beautiful lustrous plates, melts at 280°, is very pale yellow, and exhibits green fluorescence.

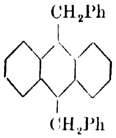
1 : 3 : 6 : 8-**Tetramethylanthraquinone** is obtained from the hydrocarbon in the usual manner. It crystallises in pale yellow prisms of m.p. 228°-230°.

2-Phenylanthraquinone (Scholl and Neovius, Ber. 44, 1075).



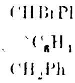
Phthalic anhydride condenses with diphenyl in presence of aluminium chloride in carbon disulphide solution, and the product is exclusively diphenyl-4-phthaloylic acid. When heated with zinc chloride at 280°, 2-phenylanthraquinone is obtained. The product is purified by reduction with alkaline hyposulphite, filtering the alkaline solution and oxidising by a current of air. The substance crystallises in yellow needles and melts at 160°-161°. The quinone may also be obtained by reducing diphenyl-4-phthaloylic acid to the corresponding diphenyl methane carboxylic acid, and this with zinc chloride at 185° is changed to 2-phenyl-9-anthrone which, on oxidation with chromic acid, yields 2-phenylanthraquinone.

9 : 10-**Dibenzylanthracene** (Lippmann and Fritsch, Monatsh. 25, 793).



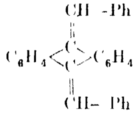
This interesting hydrocarbon is prepared by heating anthracene (100 grams), benzylchloride (145 grams), and zinc-dust (10 grams) with carbon disulphide (1 litre) on the water bath, and with continual passage of carbon dioxide, until the evolution of hydrogen chloride ceases. The substance forms blue fluorescent needles, crystallises from acetic acid and melts at 241°. It has a peculiar odour resembling carbylamine.

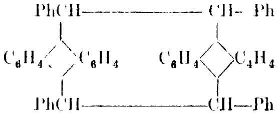
Monobromodibenzylanthracene


$$C_6H_4\overset{CHBrPh}{\underset{CH_2Ph}{\langle\;\rangle}}C_6H_4$$

This derivative is obtained by the action of bromine on dibenzylanthracene in carbon disulphide solution. The bromine is carried into the liquid mixed with carbon dioxide. The product crystallises from carbon disulphide or benzene in yellow prisms, melting, when quickly heated, at 187°.

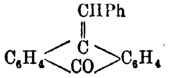
Uni- and bi-molecular **dibenzylidenedihydroanthracene**



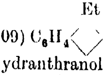


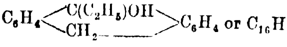
Unimolecular. Monobromodibenzylanthracene is boiled in benzene solution with aqueous potassium acetate, or the bromide is heated with a small excess of acetic anhydride. The substance melts at 234°-236°, and is soluble in chloroform with blue fluorescence.

Bimolecular $C_{56}H_{40}$. Monobromodibenzylanthracene is boiled with quinoline in benzene solution for 20 hours. It forms yellow crystals of m.p. 184° and is soluble in hot benzene or chloroform with red fluorescence. It is easily distinguished from the monomolecular compound in that its solution in sulphuric acid is green.

Benzylidene anthrone 
$$C_6H_4\overset{\overset{CHPh}{\|}}{\underset{CO}{\langle C \rangle}}C_6H_4$$

(Haller and Padova, Compt. rend. 141, 857) is closely related to the above benzal dihydroanthracenes. It is obtained by the condensation of anthranol with benzaldehyde in pyridine solution containing piperidine. The yield is 56 p.c. of that demanded by theory. The substance crystallises in yellow needles, and is readily soluble in chloroform, benzene, and acetone, sparingly so in ligroin. It melts at 126°-127°. The corresponding anisylidene and *m*-nitrobenzylidene derivatives melt at 141° and 166° respectively. The benzylidene anthrone is also easily obtained on passing hydrochloric acid into the acetic acid solution of *benzyl oxanthranol.* The latter is prepared by the action of magnesium benzyl chloride on anthraquinone. It forms colourless crystals from alcohol and melts at 146°.

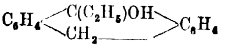
Ethylanthracene (Liebermann, Annalen, 212, 109)  is formed by boiling ethyl hydranthranol with alcohol and hydrochloric or picric acid.



$$C_6H_4\left<\begin{array}{l}C(C_2H_5)OH\\CH_2\end{array}\right>C_6H_4 \text{ or } C_{16}H_{14}.H_2O.$$

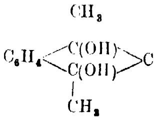
It crystallises from alcohol in large concentrically grouped plates which melt at 60°-61°. The picrate melts at 120°.

Ethylhydranthranol

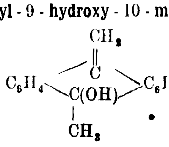


$$C_6H_4\left<\begin{array}{l}C(C_2H_5)OH\\CH_2\end{array}\right>C_6H_4$$

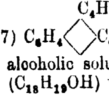
is produced by heating anthraquinone (3 parts) with zinc-dust (10 parts), caustic soda solution (10 p.c.), and ethyl bromide (2–4 parts).

9 : 10 - **Dimethyl** - 9 : 10 - **dihydroxydihydroanthracene**  (Guyot and Staehling, Bull. Soc. chim. [iii.] 33, 1152). This substance is prepared by the action of magnesium methyl iodide on anthraquinone. It crystallises from methyl alcohol in colourless prisms containing solvent of crystallisation Some of this it loses on exposure to the air, but the last molecule is not driven off unless the substance is exposed *in vacuô* to a temperature of 100°. The anhydrous compound melts at 181° and dissolves in sulphuric acid with a green colour, changing on standing to yellow. When treated with alcohols the corresponding ethers are produced. Thus ethyl alcohol yields the diethyl ether of the anthracene derivative.

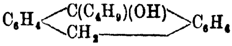
$$\begin{array}{c}CH_3\\C_6H_4\left<\begin{array}{l}C(OH)\\C(OH)\end{array}\right>C_6H_4\\|\\CH_3\end{array}$$

9 - **Methyl** - 9 - **hydroxy** - 10 - **methenedihydroanthracene**  is obtained when the dihydroxy compound (*v. supra*) is boiled with acetic acid. It is a canary yellow crystalline powder melting at 223°, and sparingly soluble in organic solvents. It dissolves in sulphuric acid to a clear yellow solution.

$$\begin{array}{c}CH_2\\ \|\\C_6H_4\left<\begin{array}{l}C\\C(OH)\end{array}\right>C_6H_4\\|\\CH_3\end{array}$$

***iso*Butylanthracene** (Liebermann, Annalen, 212, 107)  is obtained by boiling an alcoholic solution of *iso*butyl hydranthranol ($C_{18}H_{19}OH$) with picric acid or hydrochloric acid. It crystallises from alcohol in fluorescent needles; m.p. 57°. The picrate crystallises in long brownish-red needles.

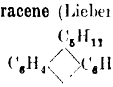
***iso*Butylhydranthranol**



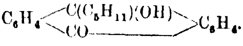
$$C_6H_4\left<\begin{array}{l}C(C_4H_9)(OH)\\CH_2\end{array}\right>C_6H_4$$

is prepared by boiling 3 parts anthraquinone with 10 parts of zinc-dust, 50 parts of caustic soda solution (10 p.c.), and 2·4 parts of *iso*butyl bromide. It crystallises in needles, which melt at 71°-72°.

***iso*Amylanthracene** (Liebermann, *l.c.*)

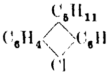


is prepared from *iso*amylhydranthranol (*v. Isobutylanthracene*). Long, colourless sea-green needles, m.p. 59°. Very soluble in benzene, CS_2,$CHCl_3$ light petroleum, and hot alcohol; difficultly soluble in cold alcohol. The solutions fluoresce blue. The solution in sulphuric acid is green; on warming it becomes red. Chromic acid oxidises it to *iso*amyloxanthranol



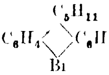
$$C_6H_4\left<\begin{array}{l}C(C_5H_{11})(OH)\\CO\end{array}\right>C_6H_4.$$

Chlor*iso*amylanthracene



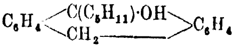
is obtained by passing chlorine into a solution of *iso*amylanthracene in chloroform. It crystallises from alcohol in pale-yellow needles, which melt at 70°-71°. The solutions fluoresce blue. The picrate crystallises in red needles, which melt at 108°.

Bromo*iso*amylanthracene



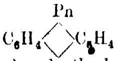
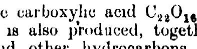
is obtained by adding the calculated quantity of bromine to the solution of the hydrocarbon in 20–30 parts of CS_2. Orange-yellow needles, m.p. 76°. The picrate crystallises in orange-yellow needles, which melt at 110°.

***iso*Amylhydroanthranol**



$$C_6H_4\left<\begin{array}{l}C(C_5H_{11})\cdot OH\\CH_2\end{array}\right>C_6H_4$$

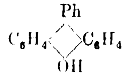
(*v. Isobutylhydranthranol*). Needles, m.p. 73°-74°. Very readily soluble in alcohol; insoluble in water.

Phenylanthracene  is obtained by distilling phenylanthrol (Baeyer, Annalen, 202, 61) $C_{20}H_{13}(OH)$ with zinc-dust; also, but in very small quantity, by distilling diphenylphthalide  or triphenylmethane carboxylic acid $C_{22}O_{16}H_2$ with zinc-dust. It is also produced, together with anthracene and other hydrocarbons, by the action of aluminium chloride on a mixture of chloroform and benzene (Friedel and Crafts, Ann. Chim. Phys. [vi.] 1, 495). It crystallises from

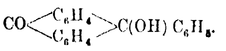
$$C_6H_4\left<\begin{array}{l}C(C_6H_5)_2\\CO\end{array}\right>O$$

alcohol in plates which melt at 151°–153°, and boil at 417°. It is readily soluble in hot alcohol, ether, CS_2, $CHCl_3$, and benzene, the solutions possessing a blue fluorescence. Oxidation with CrO_3 and acetic acid converts it into phenyloxanthranol $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(C_6H_5)OH$. The *picrate* crystallises in red needles. Reduction with hydriodic acid converts it into a dihydride $C_{20}H_{16}$, which melts at 120°–120·5°.

Phenylanthranol (Baeyer, *l.c.*)



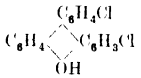
is formed by dissolving triphenylmethane carboxylic acid $(C_6H_5)_2CH{\cdot}C_6H_4{\cdot}COOH$ in 3 parts of sulphuric acid and pouring the mass into water. The precipitate is collected, washed with dilute sodium carbonate, and recrystallised from alcohol. Yellow needles, which melt at 141°–144°, with slight decomposition. It dissolves readily in ether, forming a yellowish solution, which possesses a greenish-yellow fluorescence. It dissolves also in hot alcohol, petroleum spirit, and acetone. Oxidation with CrO_3 converts it into phenyloxanthranol



$$CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OH)\,C_6H_5.$$

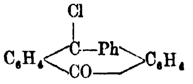
The *acetate* $C_2H_3O_2{\cdot}C_{20}H_{13}$ crystallises from alcohol in yellow needles which melt at 165°–166°.

Dichlorophenylanthranol

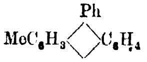


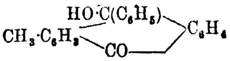
is formed by boiling phenolphthalidein chloride $CO<\begin{matrix}C_6H_4\\C_6H_3Cl\end{matrix}>C(OH)C_6H_4Cl$ with zinc-dust and acetic acid It crystallises from alcohol in needles, which melt at 170°. It is very sparingly soluble in alcohol, moderately soluble in acetone and ether, readily soluble in benzene or CS_2, forming bluish-green fluorescent solutions.

Phenyloxanthranolchloride

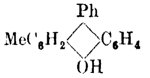


(Haller and Guyot, Bull. Soc. chim. 1897, [iii] 17, 873) is obtained by warming diphenylphthalide with phosphorus pentachloride. It crystallises from benzene in large, colourless, transparent prisms, melting at 164°. Water changes it to phenyloxanthranol, whilst with methyl alcohol it yields phenyloxanthranol methyl ether.

Methylphenylanthracene (Hemilian, Ber. 16, 2367)  is formed by the distillation of methylphenylanthranol with zinc-dust (*v. infra*). It crystallises from alcohol in yellow crystalline masses (melting-point not given). The alcoholic solution fluoresces greenish-blue. It is readily oxidised by CrO_3 and acetic acid to methylphenyloxanthranol



Methylphenylanthranol

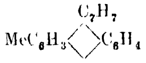


is similarly prepared by heating methyltriphenylmethane carboxylic acid

$$(C_6H_5)_2CH{\cdot}C_6H_3(CH_3)COOH$$

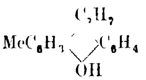
with sulphuric acid to 100°. It crystallises from alcohol in glittering plates which on heating become brown at 130°, and melt at 156°–157°. It is readily soluble in ether, boiling alcohol, and glacial acetic acid.

Methyl-*p*-tolylanthracene



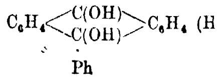
(Limpricht, Annalen, 299, 291) is obtained by the distillation of methyl-*p*-tolyloxanthranol with zinc-dust in a stream of hydrogen. It forms yellow needles of m.p. 191°. On oxidation with chromic acid in acetic acid solution, it yields methyl-*p*-tolyloxanthranol.

Methyl-*p*-tolylanthranol



This substance is easily produced by dissolving di-*p*-tolylphenyl methane *o*-carboxylic acid in concentrated sulphuric acid. On pouring the solution into water, small yellow crystals, melting at 117°, separate. The compound is easily changed to

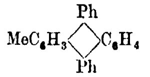
Methyl-*p*-tolyloxanthranol



by oxidation with chromic acid. This derivative crystallises from toluene in colourless needles, melting at 206°.

9 : 10 - **Diphenyl** - 9 : 10 : **dihydroxydihydroanthracene** $C_6H_4<\begin{matrix}C(OH)Ph\\C(OH)Ph\end{matrix}>C_6H_4$ (Haller and Guyot, Compt. rend. 138, 327). This compound is produced in 10 p.c. yield by the action of magnesium phenyl bromide on anthraquinone. It crystallises from methyl alcohol in colourless needles, containing solvent of crystallisation. This is lost on exposure to air, the crystals falling to a white powder, melting at 247°. The solution in sulphuric acid is indigo-blue, changing to orange-yellow on heating. The colourless solution in glacial acetic acid exhibits blue fluorescence.

2-Methyl-9 : 10-diphenylanthracene

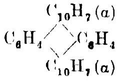


$$MeC_6H_3\langle\overset{Ph}{\underset{Ph}{\Diamond}}\rangle C_6H_4$$

(Guyot and Staehling, Bull. Soc. chim. [iii.] 33, 1104). When phenyl magnesium bromide acts on 2-methylanthraquinone the product varies according to the conditions employed. If the organo-metallic derivative is slowly added to a benzene solution of the quinone, then Hemilian's 2-methyl-9-phenyloxanthranol (*v. supra*) is the main product. On boiling the quinone with a solution of magnesium phenyl bromide for many hours, then 2-methyl-9 : 10-diphenyl - 9 : 10 - dihydroxydihydroanthracene is produced. This crystallises in cubes and melts at 240°. On treatment with zinc-dust in acetic acid solution it is reduced to 2-methyl-9 : 10-diphenylanthracene.

The latter crystallises from benzene and alcohol in yellow-green dichroic plates, melting at 213°, and soluble in organic solvents with intense violet-blue fluorescence. Chromic acid changes it to 2-methyl-9 : 10-diphenyl-9 : 10-dihydroxydihydroanthracene

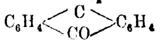
Di-α-naphthylanthracene



$$C_6H_4\langle\overset{C_{10}H_7\,(\alpha)}{\underset{C_{10}H_7\,(\alpha)}{\Diamond}}\rangle C_6H_4$$

(Guyot and Staehling, *l c*) is prepared similarly to the above diphenyl derivative. α-Naphthyl magnesium bromide and anthraquinone yield 9 : 10-di - α - naphthyl - 9 : 10-dihydroxydihydroanthracene, which forms colourless crystals from toluene, and contain 1 molecule of toluene of crystallisation. It dissolves in sulphuric acid with a malachite-green colour. Di-α-naphthylanthracene is obtained from this di-ol by reduction with zinc and acetic acid. It forms yellow crystals, soluble in benzene, and exhibiting a most intense violet fluorescence

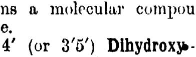
Diphenylanthrone



$$C_6H_4<\overset{\overset{Ph_2}{C}}{\underset{CO}{}}>C_6H_4$$

(Haller and Guyot, Bull. Soc. chim. 1897, [iii.] 17,873). This compound is obtained by the action of aluminium chloride on a benzene solution of phthalyltetrachloride. The latter may be replaced by anthraquinone chloride or phenyloxanthranol chloride, which are probably intermediate products of the reaction. The substance crystallises from acetic acid in colourless needles, or from benzene in large transparent prisms, melting at 192°. Although undoubtedly a ketone, it does not react with phenylhydrazine. It forms a molecular compound with nitrobenzene.

2′ : 4′ (or 3′5′) **Dihydroxy- 9 : 9 - diphenylanthrone**

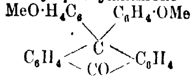


$$C_6H_4<\overset{\overset{PhC_6H_3(OH)_2}{C}}{\underset{CO}{}}>C_6H_4$$

(Liebermann and Lindenbaum). Phenyloxanthranol chloride (*v supra*) furnishes this substance when it is treated with resorcinol in boiling benzene solution. Other phenols react similarly. The resorcinol derivative crystallises from alcohol in the form of colourless needles, which, when heated, lose solvent at 125°, and then melt at 259°-261°. The solution in concentrated sulphuric acid is yellow. On boiling with acetic anhydride and sodium acetate a diacetate is produced, and this compound crystallises from alcohol in plates and melts at 191°.

Scharwin and Kusnezof (Ber. 36, 2020) have condensed anthraquinone with phenols and with resorcinol, using for the former condensation, tin tetrachloride, and for the latter, zinc chloride. The substances produced are hydroxy derivatives of diphenylanthrone.

p-**Dimethoxydiphenylanthrone**

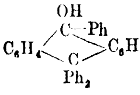


$$C_6H_4<\overset{\overset{MeO\cdot H_4C_6\quad C_6H_4\cdot OMe}{C}}{\underset{CO}{}}>C_6H_4$$

(Scharwin, Naumof and Sandurin).

Anthraquinone chloride condenses with anisole to form this substance, when the solution of the mixture in carbon disulphide is treated with aluminium chloride. It crystallises from alcohol in yellow rhombohedra of m.p. 208°. It is soluble in the usual organic solvents, and in sulphuric acid with red-violet colour. On hydrolysis with aluminium chloride it yields phenolanthraquinone identical with the product obtained by Scharwin and Kusnezof (*l.c.*) from anthraquinone and phenol.

9 : 10 : 10 - **Triphenyl - 9 - hydroxydihydroanthracene**

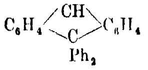


$$C_6H_4<\overset{\overset{OH}{C-Ph}}{\underset{\underset{Ph_2}{C}}{}}>C_6H_4$$

(Haller and Guyot, Compt. rend. 139, 9). This substance can be obtained by dropping a benzene solution of diphenylanthrone (*v. supra*) into an ethereal solution of magnesium-phenyl bromide. After the addition of water, and acidification, the solvent is evaporated, when the carbinol crystallises in colourless voluminous needles, which contain 1 molecule of ether of crystallisation. This is removed at 120°, and the substance then melts at 200°. It dissolves in sulphuric acid with orange-red colour.

The methyl ether is obtained by adding methyl alcohol containing hydrochloric acid to the boiling toluene solution of the carbinol. The colourless leaflets melt at 218°. The corresponding ethyl ether melts at 250°.

Triphenyldihydroanthracene

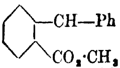


$$C_6H_4<\overset{\overset{Ph}{CH}}{\underset{\underset{Ph_2}{C}}{}}>C_6H_4$$

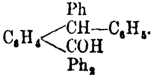
is prepared—

(*a*) By boiling the above carbinol or its ethers with zinc-dust and acetic acid.

(*b*) Methyltriphenylmethane-*o*-carboxylate



reacts with magnesium-phenyl bromide, yielding the tertiary alcohol and

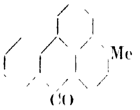


$$C_6H_4<\begin{matrix}\overset{Ph}{CH}-C_6H_5\\ \underset{Ph_2}{COH}\end{matrix}.$$

This crystallises from methyl alcohol as its methyl ether, m.p. 215°. The orange-red solution of this methoxyl compound in sulphuric acid quickly becomes colourless, and on dilution triphenyldihydroanthracene is precipitated. This last change is still better effected by the agency of hydrochloric acid in glacial acetic acid solution.

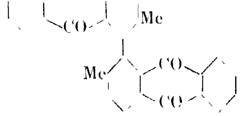
Triphenyldihydroanthracene forms colourless crystals from a mixture of benzene and alcohol, and melts at 220°. Its solution in sulphuric acid is colourless.

Methylbenzanthrone.

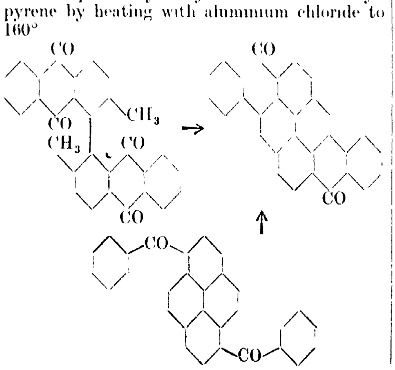


β-Methylanthranol dissolved in sulphuric acid (62° Bé) is heated with glycerol at 145°–150° (D. R. P. 200335). This homologue of benzanthrone dissolves in concentrated sulphuric acid to a red-brown solution which exhibits orange fluorescence. It crystallises from alcohol in yellow needles which melt at 199°. On heating with concentrated alcoholic potassium hydroxide at 190° it yields a vat dyestuff giving lilac shades (D. R. P. 188193). With sulphur at 240° it reacts with production of a bluish-green vat-dyestuff (D. R. P. 209351).

2 : 2′-Dimethyl-1 : 1′-Dianthraquinonyl,



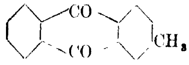
This important intermediate was first obtained by Scholl and Mansfield (Ber. 1907, 40, 1691) in the course of their work on the constitution of flavanthrene, pyranthrene, and other complex polynuclear vat-dyestuffs. It is prepared from 1-iodo-2-methylanthraquinone by the action of copper powder (*cf.* also D. R. P. 180157). Another method (D. R. P. 184495, 215006) consists in treating the diazonium sulphate from 1-amino-2-methylanthraquinone with copper powder in acetic anhydride solution or with cuprous chloride in aqueous solution. Condensation by heating or in various other ways produces pyranthrone (Indanthrene Gold-Orange G) (*see* VAT-DYES) in regard to which it may be mentioned here that its constitution is further proved by the synthesis from dibenzoylpyrene by heating with aluminium chloride to 160°



This is an elegant example of the synthesis of a complex substance by two entirely different methods and is a striking instance of the value of structural formulæ. Halogenated pyranthrenes give redder shades, and a number of these are known and obtained by direct halogenation, or, more usually, from halogenated dimethyldianthraquinonyls. It should be noted that Auranthrone, a vat-dyestuff obtained from 2-methylanthraquinone by heating with alcoholic potassium hydroxide is possibly dianthraquinonylethylene.

METHYLANTHRACENE DERIVATIVES OCCURRING IN NATURE.

Chrysophanic acid (*Chrysophan, Chrysophanol*)



Occurrence.—In various species of lichens, *Parmelia parietina* (Ach.), *Lecanora* (*Placodium*) *elegans* (Ach.), *Cassia speciosa* (Schrad.), *Rhamnus frangula* (L.), *Rhamnus Purshiana* (D.C.), (as glucoside), in the root of *Rumex obtusifolius* (L.), in senna leaves, and in Chinese rhubarb. From this latter source a definite glucoside chrysophanein $C_{21}H_{20}O_9$ has been isolated by Gilson (Arch. internat. de Pharmako-dynamie et de Therapie, 1905, vol. 14, 487).

Preparation.—Chrysophanic acid is usually obtained by the oxidation of chrysarobin (*v. infra*) (Liebermann, Seidler, Annalen, 212, 36), which is mixed with dilute potassium hydroxide solution and a current of air passed until the liquid has acquired a deep reddish colour. The quinone is precipitated into HCl and extracted with ligroin (b.p. 50°–60°). On evaporation of the solvent a yellow residue is obtained which can be crystallised from alcohol. Fischer and Gross (J. pr. Ch. 1911, [ii.] 84, 370) give details of the preparation of chrysophanic acid by oxidation of chrysarobin by chromic acid in glacial acetic acid solution. The melting-points found for chrysophanic acid by various authors range from 154° to 190°, and this has been shown to be due to the fact that the substance commonly contains an admixture of its methyl ether. Repeated crystallisation leads to a product containing only 0·36 p.c. methoxyl, and this melts at 188°. Oesterle (Arch. Pharm. 243, 434) obtained a methoxyl free chrysophanol by treatment with anhydrous aluminium chloride in benzene solution. After crystallisation from ligroin, alcohol, and benzene, the pure chrysophanol melted at 196°. This melting-point was also found by Gilson (*l.c.*) for the hydrolysis product of the pure glucoside chrysophanein. The analysis of the pure substance agreed excellently with the formula $C_{15}H_{10}O_4$. As ordinarily obtained chrysophanol crystallises in orange needles, which sublime, partially with decomposition, in the same form. The methoxyl free substance consists of shining brown-yellow leaflets, when crystallised from benzene. It is almost insoluble in water, but soluble in ether, benzene, and glacial acetic acid. It is difficultly soluble in ammonia and alkaline carbonates, but readily so in potassium hydroxide, forming a deep-red solution. Distilled with zinc-dust chrysophanic acid yields methylanthracene (Liebermann, Annalen, 183, 169).

The absorption spectrum of a solution of chrysophanic acid (Liebermann and Kostanecki, Ber. 19, 2330) in sulphuric acid, which resembles very closely that of chrysazin, is shown in Fig. 4.

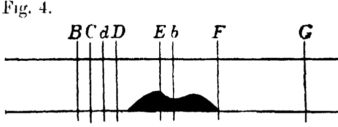


FIG. 4.

Since chrysophanic acid diacetate is converted by oxidation, with chromic acid in acetic acid and acetic anhydride solution, into diacetyl rhein, the positions of the groups are evidently identical in the two substances.

Derivatives of chrysophanic acid. *Tetranitrochrysophanic acid* (Liebermann and Giesel, Annalen, 183, 175) is obtained when chrysophanic acid is warmed with concentrated nitric acid. It occurs in yellow micro leaflets, which decompose on heating. The substance is quite insoluble in water, soluble in acetic acid, and behaves as a strong acid. It resembles chrysammic acid.

Amino derivatives. *Aminodeoxychrysophanic acid* (Liebermann and Giesel, *l.c.*) was obtained by heating chrysophanic acid with concentrated ammonia at 200°, or by leaving the acid with strong ammonia for a long time at the ordinary temperatures (Hesse, Annalen, 309, 32). It is a cherry-red powder forming easily soluble purple-violet salts with alkalis. It is sparingly soluble in ether, comparatively readily so in alcohol. In this compound, either one of the hydroxy groups of the chrysophanic acid is replaced by amino, or one of the carbonyl oxygens by imino.

Diamino-de-dioxy-chrysophanic acid (Liebermann and Giesel, *l.c.*) is obtained when chrysophanic acid is heated at 150° with a small quantity of aqueous ammonia. Since this substance is soluble in alkalis it may probably be more correctly designated as diiminochrysophanic acid. On boiling with acetic anhydride it yields acetylchrysophanic acid imide (so called) having the composition $C_{15}H_8(C_2H_3O)NO$. This substance crystallises from chloroform in violet needles, having a metallic reflex.

Monoacetylchrysophanic acid $C_{15}H_9(C_2H_3O)O_4$ (Hesse, *l.c.*) is obtained by the action of acetic anhydride on chrysophanic acid. It is dissolved by gently warming and then allowed to remain 48 hours. It crystallises from acetic acid in yellow needles of m.p. 152°.

Diacetylchrysophanic acid $C_{15}H_8(C_2H_3O)_2O_4$ (Liebermann, *l.c.*) is the product when chrysophanic acid is boiled with sodium acetate and acetic anhydride. Oesterle (*l.c.*) gives the melting-point of the pure substance as 208°. It crystallises in light yellow leaflets, and can be oxidised by chromic acid to diacetyl rhein (Fischer, Falco and Gross, J. per Chem. 1911, [ii.] 83, 208).

Dibenzoylchrysophanic acid $C_{15}H_8(C_7H_5O)_2O_4$ (Warren de la Rue and Müller, J. 1862, 323) obtained by the Schotten-Baumann reaction, crystallises in pale yellow needles, melting at 200°–208° (Tutin and Clewer, Chem. Soc. Trans. 99, 956).

Chrysophanic acid monomethyl ether

$$C_{15}H_8O_2(OH)(OCH_3)$$

(Oesterle, *l.c.*) is the main product when chrysophanic acid is methylated by means of methyl sulphate and potassium hydroxide. After a process of purification, it can be crystallised from alcohol. It forms clear orange needles which melt at 204°. Its acetyl derivative consists of lemon-yellow needles when crystallised from alcohol, m.p. 204°.

Chrysophanic acid dimethyl ether

$$C_{15}H_8O_2(OCH_3)_2$$

is also produced when the acid is treated with a large excess of methyl sulphate and alkali. It crystallises in orange needles, m.p. 195°, either from acetic acid or aqueous alcohol. It dissolves with red colour in concentrated sulphuric acid.

Chrysophanein (Gilson, *l.c.*) is as already mentioned the glucoside of chrysophanic acid. It crystallises in needles from 92 p.c. alcohol and melts at 242°–249°. It is tasteless, and this in conjunction with its other properties renders the formulation of barbaloin as a glucoside of aloemodin and arabinose open to criticism.

Chrysophanhydranthrone $C_{15}H_{12}O_3$. Since chrysarobin (*see* below) gave chrysophanic acid on oxidation, attempts were made to realise the reverse process. Liebermann (Ber. 21, 436) reduced chrysophanic acid with tin and hydrochloric and acetic acids, and obtained a compound which crystallised from benzene in yellow leaflets and melted at 196°. It was not chrysarobin and was termed chrysophanhydranthrone. Hesse (Annalen, 284, 194) obtained the same substance by heating chrysophanic acid with hydriodic acid. Jowett and Potter (Chem. Soc. Trans. 1902, 1584) obtained in this reaction chrysarobin; but Hesse obtained chrysophanhydranthrone by heating chrysarobin with concentrated hydrochloric or hydriodic acid. The melting-point of the pure hydranthrone is 205°–210°. On distillation with zinc-dust β-methylanthracene is obtained. It yields a diacetyl derivative which crystallises from acetic acid in needles of m.p. 238°–240°.

Chrysarobin $C_{15}H_{12}O_3$ (?). This derivative of chrysophanic acid is a remedy indispensable to the dermatologist, and was first obtained from Goa powder by Attfield (Pharm. J. 5, 721) by extraction with chloroform. Liebermann and Seidler (Annalen, 212, 34) prepared the compound in a pure condition. The so-called Goa powder separates out in the pith hollows of certain trees belonging to the genus *Andira* in Brazil and India. It is extracted with benzene, the solution evaporated, and the residue repeatedly crystallised from glacial acetic acid. Small yellow needles, m.p. 170°–178°. Insoluble in water and ammonia, difficultly soluble in alcohol and ether, more readily soluble in benzene, glacial acetic acid, and chloroform. Insoluble in very dilute potassium hydroxide, but soluble with a dark green fluorescence in strong solutions. This solution is readily oxidised by the oxygen of the air, yielding chrysophanic acid. Distilled with zinc-dust, chrysarobin yields methyl anthracene. Chrysarobin has no dyeing properties. It may be the anthranol of chrysophanic acid, although a double molecular formula has been ascribed to it by several authors.

The acetyl derivatives of chrysarobin and of the dichrysarobin obtained by heating the solution in acetic acid have been carefully investigated by Hesse (Annalen, 309, 60).

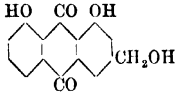
Monoacetyl derivative is obtained by 3 4 hours' boiling with acetic anhydride The yellow leaflets obtained on crystallisation from acetic acid melt at 188°-190°.

Diacetyl derivative is produced when chrysarobin is boiled 6 hours with acetic anhydride. It crystallises in rhombic prisms, m.p. 216°; the solutions fluoresce blue. A β-diacetate of m.p. 265°-270° has also been isolated.

Triacetyl chrysarobin can be prepared by heating either chrysarobin or chrysophanhydranthrone with acetic anhydride and sodium acetate for 1 hour. It crystallises in prisms, m.p. 234°.

Hexaacetyl dichrysarobin is produced by boiling chrysarobin with sodium acetate and acetic anhydride for many hours. It is amorphous, and melts at 125°.

Aloemodin



Aloemodin occurs (Léger, Bull. Soc. chim. [iii.] 23, 785) together with barbaloin and *iso*-barbaloin in Barbados aloes, and in smaller quantities in all other varieties of aloe.

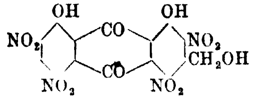
It may be prepared best by the action of alcoholic hydrochloric acid on barbaloin (Oesterle, Arch. Pharm. 237, 699). The dried reaction product is extracted with hot toluene, the solution treated with animal charcoal and concentrated; when on cooling orange-yellow needles separate. The substance is purified by many recrystallisations from toluene and from acetic acid. After sublimation the pure aloemodin melts at 224°. Léger, and Jowett and Potter have obtained aloemodin by the oxidation of barbaloin with sodium peroxide. Tetrachloraloemodin and tetrabromaloemodin are produced by the oxidation of tetrachlor- and tetrabrombarbaloins with the same reagent.

When heated with a little sulphuric acid and subsequently treated with dilute ammonia solution, aloemodin gives a violet colour; frangula emodin under the same conditions gives a cherry-red. Aloemodin when oxidised with chromic acid in acetic acid solution yields rhein $C_{15}H_8O_6$. This is a carboxylic acid, so that aloemodin $C_{15}H_{10}O_5$ must be recognised as the corresponding primary alcohol, and further as hydroxychrysophanic acid.

Diacetylaloemodin $C_{15}H_8O_5(COCH_3)_2$ is obtained by boiling aloemodin with acetic anhydride and sodium acetate for an hour. It crystallises from acetic acid in small yellow needles, m.p. 177°-178°. Although aloemodin yields a diacetate, tetrachloraloemodin has three hydroxyl groups which can be acetylated.

Tribenzoyl aloemoin $C_{15}H_7O_5(COPh)_3$ is obtained by the Schotten-Baumann reaction. It crystallises well from ethyl acetate as greenish-yellow micro leaflets, m.p. 235°.

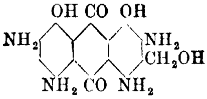
Tetranitroaloemodin



is the so-called *aloetic acid*, which is obtained together with chrysammic acid, by the action of nitric acid on barbaloin. The substance was first obtained by Scheele, who termed it aloë bitter, and subsequently by a number of chemists, but it was first isolated in the pure condition by Mulder (Annalen, 1849, 72, 286). Oesterle proved that the substance is tetranitroaloemodin since he applied to it the process by which Liebermann and Giesel (Annalen, 183, 184) converted chrysammic acid into chrysazin, and obtained aloemodin.

Aloetic acid is a yellow crystalline powder which becomes red on standing in the air. It is fairly soluble in water to an intense red solution It is also soluble in ether, chloroform, alcohol, benzene, and ethyl acetate. Léger (Compt. rend. 1911, 153, 114) finds that on further oxidation with nitric acid, aloetic acid yields chrysammic acid and 2 : 4 : 6 trinitrometahydroxybenzoic acid.

Hydroaloetic acid



The reduction of aloetic acid (Oesterle, Schweizer Wochenschr. f. Ch. u. Ph. 1906, No. 31) is accomplished by an aqueous solution of potassium hydrogen sulphide. Hydroaloetic acid is a blue-black amorphous substance very sparingly soluble in most solvents. The solution of the substance in concentrated sulphuric acid was treated with nitrous fumes and then boiled with an excess of alcohol. It was found possible to isolate aloemodin by acetylating the product, purifying the diacetate and hydrolysing with alcoholic potash. The aloemodin obtained melted at 223°.

Frangula emodin (emodin)

$$C_{15}H_{10}O_5, \text{ or } C_{14}H_4(CH_3)(OH)_3O_2$$

(position of OH groups unknown, but probably the same as those in flavopurpurine).

Occurrence.—In rhubarb root, the bark of the alder tree, in *Rhamnus Purshiana* (D.C.) (cascara sagrada) and *Rhamnus cathartica* (Linn.).

Preparation.—Alder bark is extracted with dilute sodium hydroxide, the solution precipitated with HCl, and the precipitate purified by repeated recrystallisation from absolute alcohol.

Orange-red, silky needles, m.p. 245°-250° (Liebermann, Annalen, 183, 161).

Moderately soluble in benzene, more readily so in alcohol and acetic acid; soluble in dilute ammonia, forming a cherry-red solution. Does not dye mordanted cloth. Distilled over zinc-dust β-methylanthracene results. The absorption spectrum of a solution in concentrated sulphuric acid is shown in Fig. 5 (Liebermann and Kostanecki, Ber. 19, 2330):

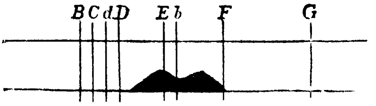


FIG. 5.

and closely resembles that of flavopurpurin

The triacetate (Liebermann, *l.c.*)

$$C_{15}H_7(C_2H_3O)_3O_5$$

crystallises from acetic acid in yellow needles, m.p. 190°.

Tribenzoate. Tutin and Clewer (Chem. Soc. Trans. 99, 954) obtained this derivative by applying the Schotten-Baumann reaction to emodin. It crystallises from glacial acetic acid in small pale yellow needles, and melts at 186°.

Dibenzoyl emodin, m.p. 225°, has also been described, but there appears to be some uncertainty as to its existence.

Emodinmonomethyl ether

$$CH_3{\cdot}C_{14}H_4O_2(OH)_2OCH_3$$

was found by Perkin and Hummel in *Ventilago maderaspatana* (Chem. Soc. Trans. 65, 940), by Tutin and Clewer in rhubarb root and in *Rumex Ecklonianus* (Meissn.), whilst Oesterle and Johann (Arch. Pharm. 1910, 248, 476) show that it is the methylated compound usually associated with chrysophanic acid.

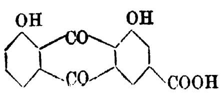
Jowett and Potter (Chem. Soc. Trans. 1903, 77, 1330) obtained the substance by heating the potassium salt of emodin with methyl iodide. It crystallises from benzene in long, orange-red needles, m.p. 200°. It is sparingly soluble in alcohol or acetone. A nitro derivative melts at 217°, and a tetranitro derivative at 275° with decomposition. The former is obtained by using nitric acid of sp gr. 1·42, the latter when nitric acid (sp.gr. 1·54) is employed.

Its diacetate crystallises in golden needles, m.p. 185°, and the dibenzoate prepared by the Schotten-Baumann method melts at 228°.

Emodin trimethyl ether has been prepared by methylation of emodin with dimethyl sulphate and aqueous potassium hydroxide. It crystallises in yellow needles melting at 225° (Oesterle and Tisza, Archiv. d. Pharm. 1908, 246, 112).

Frangulin. This emodin derivative was first obtained in a pure condition by Casselmann (Annalen, 104, 77), although Binswanger (Report, Pharm. 104, 151) had previously obtained it in a crude state from the bark of *Rhamnus frangula* (Linn.). It crystallises from alcohol in lemon-yellow, silky needles, melting at 226°. Acids hydrolyse it with formation of emodin and rhamnose so that the body is a rhamnoside of emodin. Its precise composition is at present uncertain. *Polygonin* is another glucoside of emodin, although the nature of the sugar is unknown. It was extracted by A. G. Perkin from *Polygonum cuspidatum* (Sieb. et Lucc). (Chem. Soc. Trans. 67, 1084). It crystallises in slender, orange-yellow needles, m.p. 202°–203°.

Rhein



Rhein occurs in rhubarb, from which it was first isolated by Hesse (Annalen, 1899, 309, 43). He gave it the formula $C_{15}H_{10}O_6$, and considered it a tetrahydroxymethylanthraquinone. Tschirch and Heuberger (Arch. Pharm. 1902, 240, 611), however, made analyses from which they concluded that rhein is $C_{15}H_8O_6$, and since only a diacetate could be prepared, they assigned to the substance the constitution of a methylene ether of a tetrahydroxyanthraquinone. In support of this view it was also urged that on distillation with zinc-dust rhein yields anthracene. Oesterle and Tisza (Schweiz. Woch. Chem. Pharm. 1908, 46, 701) carefully purified rhein, by crystallisation from pyridine, and sublimation in cathode ray vacuum, and support the empirical formula of Tschirch and Heuberger. Rhein is best prepared by the oxidation of barbaloin or the acetyl derivative of barbaloin. Oesterle (Schweiz. Woch. f. Chem. Pharm. 1903, 50) obtained a small yield by oxidising barbaloin with chromic acid in aqueous solution, but when tetraacetylbarbaloin is oxidised with chromic acid in acetic anhydride solution, a 50 p.c. of diacetylrhein is easily obtained, and rhein is thus shown to be a dihydroxyanthraquinone carboxylic acid (Robinson and Simonsen, Chem. Soc. Trans. 95, 1085). Rhein crystallises from pyridine in combination with a molecule of the solvent in glistening orange needles. These fall to a powder at 130°, and the pure rhein then melts at 318° (Tutin and Clewer, *l.c.*). Oesterle's purest rhein melted at 321°–321·5°. It is sparingly soluble in organic solvents, but dissolves readily in sodium carbonate solution. It dyes both mordanted and unmordanted wool clear yellow shades.

Diacetate. Various melting-points have been assigned to this substance ranging from 236° to 258°. The latter value is probably correct, and was obtained by Tutin and Clewer (*l.c.*), who prepared this derivative by heating rhein with a large excess of acetic anhydride and a little camphor sulphonic acid. After concentration the compound separates in rosettes of pale yellow needles, m.p. 258°. It is soluble in sodium carbonate solution, and on hydrolysis with alcohol and sulphuric acid yields the ester of rhein.

Dibenzoyl rhein (Tutin and Clewer, *l.c.*) obtained by the Schotten-Baumann reaction, crystallises from acetic acid in yellow brown prisms, m.p. 262°.

Rhein methyl ester $C_{14}H_5O_2{\cdot}(OH_2){\cdot}CO_2Me$ (Robinson and Simonsen, *l.c.*) forms deep orange needles by crystallisation from methyl alcohol, and melts at 174°. It is insoluble in sodium carbonate solution.

Rhein ethyl ester $C_{14}H_5O_2{\cdot}(OH_2){\cdot}CO_2Et$ is obtained by esterifying either rhein or diacetyl rhein with alcohol and sulphuric acid. Orange needles from alcohol, m.p. 159°. It yields a diacetate, melting at 170°, which is quite insoluble in cold aqueous potash.

Dimethylrhein $C_{14}H_5O_2(OMe)_2COOH$ (Robinson and Simonsen, *l.c.*) is prepared by treating an alkaline solution of rhein with methyl sulphate in the cold. The substance was isolated by means of its sparingly soluble potassium salt. It crystallises from alcohol in light brown needles, and melts when pure at 283°–284°. It dissolves in alkali to orange-yellow solutions, and can be neither acetylated nor benzoylated. Its ethyl ester melts at 185°–187°, and is insoluble in alkalis.

Dimethyl rhein chloride $C_{14}H_5O_2(OMe)_2COCl$ is produced from the acid by the action of thionyl chloride. It is crystallised by adding ligroin to its solution in chloroform. Canary-yellow prisms melting at 190° are obtained. On treatment with ammonia—

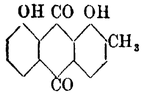
Dimethyl rhein amide

$$C_{14}H_5O_2(OMe)_2{\cdot}CO{\cdot}NH_2$$

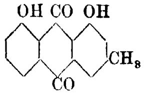
is obtained. This very insoluble substance can be crystallised from a large quantity of ethyl acetate. It occurs in microscopic hexagonal plates, m p. 287°. It is a fact of great importance that this amide undergoes the Hofmann reaction, and can be converted in this way into an aminodimethoxyanthraquinone, which, after removal of the amino group and demethylation, yields chrysazin. Rhein is thus chrysazin carboxylic acid.

Constitution of Chrysophanic Acid, Aloemodin, and Rhein.

The relationship of chrysophanic acid, aloemodin, and rhein is expressed by the scheme, RCH_3, $RCH_2{\cdot}OH$, $RCOOH$, since both chrysophanic and aloemodin yield rhein on oxidation and rhein is a carboxylic acid (Robinson and Simonsen, *l.c.*). Now chrysophanic acid is derived from β-methylanthracene whilst rhein can be degraded to chrysazin. Accepting the usual 1 : 8-configuration for chrysazin, this leaves two possible formulæ for chrysophanic acid, namely—



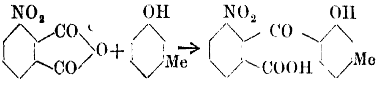
and



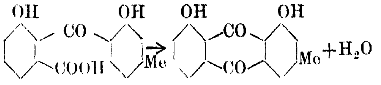
That the latter (and therefore the corresponding formulæ for aloemodin and rhein) must be taken as correct is proved by the fact that aloetic acid (*see* above) is oxidised by nitric acid with formation of 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid.

Furthermore, Léger (C. R. 1912, 154, 281) has found that chrysophanic acid on fusion with potash yields 5-hydroxyisophthalic acid. All possible doubt has been removed by the following:

Synthesis of Chrysophanic acid (Eder and Widmer, Helv. Chim. Acta, 1922, 5, 3). *a*-Nitrophthalic anhydride condenses with *m*-cresol in presence of aluminum chloride to *3-nitro-o-2′-hydroxytoluoylbenzoic* acid.



This is reduced to the corresponding amino-acid by means of ferrous hydroxide in ammoniacal solution and then converted through the diazo-derivative into 3-hydroxy-*o*-2′-hydroxy-*p*-toluoylbenzoic acid. The latter yields chrysophanic acid, m.p. 193°–194°, identical with the natural product, on treatment with a mixture of boric and sulphuric acids at 160°–170°.



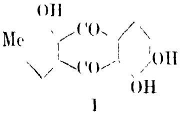
The proof is conclusive since the anthrarufin derivative which might have been obtained in this synthesis was prepared in another way.

In view of the fact that aloin yields a pentose and aloemodin on hydrolysis and the latter may be oxidised to rhein or reduced to chrysophanic acid (Oesterle, Arch. Pharm. 1911, 249, 445) it is remarkable that Seel, Kelber and Scharf (Ber. 1917, 50, 759) should be able to isolate a tetrahydroxymethylanthraquinone by oxidation of aloin with Caro's acid. This substance melts at 232°–234° and forms a tetraacetate, m.p. 198°–201°, and tetrabenzoate, m.p. 236°–238°. It seems very probable that this compound is a hydroxyaloemodin and has one hydroxyl in the side-chain.

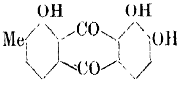
Rubiadin. This substance, isolated by Schunck (Phil. Trans. 1853, 72) and investigated by Schunck and Marchlewski (T. 1893, 63, 973; 1894, 65, 183) is obtained as a glucoside from madder of Dutch origin and appears to be 2 : 4 - dihydroxy - 1 - methylanthraquinone. It crystallises from benzene in yellow needles, melting at 290°, and forms an acetate melting at 225°.

Barrowcliff and Tutin (T. 1907, 91, 1913) have identified a constituent of Morinda longiflora as a hydroxymethoxymethylanthraquinone which on complete methylation yields 1 : 3-dimethoxy-2-methylanthraquinone. The latter crystallises in golden needles melting at 181°. On the other hand, Simonsen (T. 1920, 117, 561) points out that this constituent is the monomethyl ether of rubiadin and may be hydrolysed to rubiadin (m.p. 290°; acetate, m p. 225°) by heating with concentrated hydrochloric acid in a sealed tube at 140°–150°.

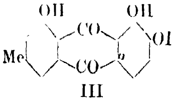
Morindone (*see* Morinda citrifolia) is a trihydroxymethylanthraquinone, considered by Simonsen (T. 1918, 113, 766) to be a hydroxy-β-methylchrysazin (I) or a hydroxy-β-methylanthrarufin (II), but the grounds for rejecting one of the formula (III) or (IV) which are hydroxychrysophanic acids are not very convincing.



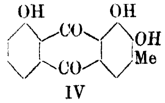
I



II



III

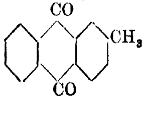


IV

W. H. P. and R. R.

METHYLANTHRANILIC ACID *v.* Amino-acids (Aromatic).

2-METHYLANTHRAQUINONE



Obtained by heating phthalic anhydride with toluene in presence of aluminium chloride, steam-distilling to remove excess of toluene, adding sodium carbonate, filtering and precipitating the 2-*p*-toluoyl-benzoic acid by acid, redissolving in fuming sulphuric acid, heating and pouring into water when 2-methylanthraquinone is precipitated. Pale yellow needles, m.p. 177°. Soluble in acetic acid or benzene.

METHYLARBUTIN *v.* GLUCOSIDES.

METHYLASPIRIN *v.* SYNTHETIC DRUGS.

METHYLATED SPIRIT *v.* ALCOHOL.

METHYLAURIN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

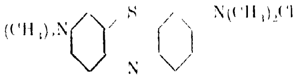
α-METHYLBUTYRIC ACID *v.* VALERIC ACIDS.

METHYLDIBUTYLACETIC ACID *v.* HENDECATOIC ACIDS.

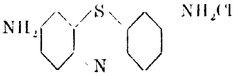
METHYLDIETHYLACETIC ACID *v.* HEPTOIC ACIDS.

METHYLDIPHENYLAMINE *v.* DIPHENYLAMINE.

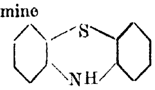
METHYLENE BLUE



A colouring matter first obtained by Caro in 1876 by the oxidation of dimethyl *p*-phenylenediamine in presence of sulphuretted hydrogen. By treating *p*-phenylenediamine with sulphuretted hydrogen and oxidising agents, or by heating it with sulphur and subsequently oxidising, Lauth obtained a violet basic colouring matter containing sulphur, known as 'Lauth's violet' or thionine.



The comparatively small yield of the colouring matter (15–20 p.c. of the *p*-phenylenediamine taken), together with the difficulties attending the preparation of the materials required, prevented its manufacture on the large scale. Lauth's reaction, however, became of industrial importance through Caro's discovery of the method of manufacture of nitrosodimethylaniline whereby it was readily possible to obtain dimethyl-*p*-phenylenediamine. This compound, when treated by Lauth's reaction, gave rise to a methylated Lauth's violet, which differed from the parent substance in being of a pure blue colour, and also in being more easily obtained and in much larger quantity. The new colouring matter came into commerce under the name of *Methylene blue*.[1] Its constitution, together with its relation to Lauth's violet (thionine) was first established by Bernthsen (Annalen, 1885, 230, 73). He showed that both these substances were derived from thiodiphenylamine



from which by nitration, reduction, and subsequent oxidation, Lauth's violet could be obtained, methylene blue being the tetramethyl derivative.

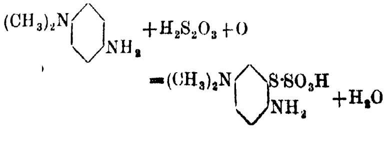
The method of manufacturing methylene blue formerly adopted by the Badische Anilin und Soda-fabrik (Eng. Pat. 3751, 1887; D. R. P. 1886; U.S. Pat. 204796; *cf.* also Eng. Pat. 4048, 1882; D. R. P. 24125; Muhlhäuser, Dingl. poly. J. 1886, 262, 371) consists in reducing nitrosodimethylaniline $NO\cdot C_6H_4\cdot H(CH_3)_2$, made by the action of sodium nitrite on dimethylaniline by means of zinc or sulphuretted hydrogen; the dimethyl *p*-phenylenediamine so obtained is treated in dilute acid solution with sulphuretted hydrogen and some oxidising agent (*e.g.* ferric chloride)

$$2C_8H_{12}N_2+H_2S+3O+2HCl$$
$$=C_{16}H_{18}N_3SCl+NH_4Cl+3H_2O$$

By the gradual addition of the ferric chloride the liquid becomes deep blue, and the resulting colouring matter is 'salted out' by adding common salt and zinc chloride, and purified by re-solution in water and 're-salting out.' This double salt, which constitutes the methylene blue of commerce, crystallises in copper-coloured crystals, readily soluble in pure water, but sparingly soluble in solution of zinc chloride.

Tetramethyldiaminodiphenylamine when oxidised in presence of sulphuretted hydrogen yields only traces of methylene blue. Similarly in the simultaneous oxidation of dimethyl-*p*-phenylenediamine and dimethylaniline in presence of sulphuretted hydrogen, the dimethylaniline enters but slightly into the reaction. On the other hand, if the tetramethyldiaminodiphenylamine, or the mixture of dimethyl-*p*-phenylenediamine and dimethylaniline, is oxidised in presence of sodium thiosulphate, a peculiar sulphoacid results, which on boiling with acids decomposes into sulphur dioxide and *leuco-methylene blue*. By the oxidation of this body methylene blue is readily obtained (Ulrich, Eng. Pat. 43, 1886; D. R. PP. 38573, 39757). According to D. R. P. 38573 a mixture of the neutral salts of aminodimethylaniline and dimethylaniline is oxidised in presence of the thiosulphate; in No. 39757, a solution of nitrosodimethylaniline hydrochloride is heated with dimethylaniline and sodium thiosulphate.

The process by which methylene blue is now manufactured (Eng. Pat. 10314, 1888; 8221, 1893; *D. R. PP. 45839, 46085, 47374. See also* Fr. Pat. 122720, 173137, 181827; U.S. Pat. 270311, 363592, 366639, 366640, 384480) is as follows: *p*-aminodimethylaniline (dimethyl-*p*-phenylene-diamine) is mixed with sodium thiosulphate and the mixture oxidised by potassium dichromate to the thiosulphonic acid, thus—



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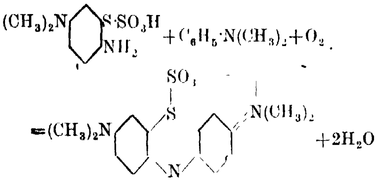
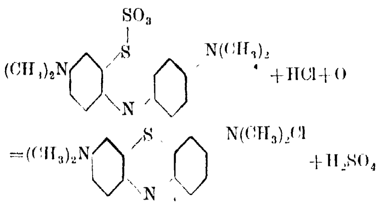
[1] Methylene blue appears on the market under this name and also with the following marks: 2B (Badische Co.); 2B powder extra (Berlin Co.); BG conc. zinc salt (Ter Meer); 4BE (Poirrier). It is manufactured in England by British Dyes, Ltd., and L. B. Holliday and Co., Huddersfield, by Claus and Co., Ltd., Manchester, and by several firms in America.

Dimethylaniline is added and the indamine is formed by oxidation with dichromate



The indamine is now boiled with dilute acid or zinc chloride solution whereby the colouring matter is formed



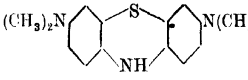
A solution of *p*-aminodimethylaniline hydrochloride (about 250 litres), prepared by converting 6 kilos. of dimethylaniline into nitrosodimethylaniline hydrochloride and reducing this with zinc-dust, is neutralised at 18°–20° with sodium hydroxide solution until a faint turbidity is produced. 16 kilos. of aluminium sulphate are now added, the mixture stirred for half an hour and then a concentrated solution of 13 kilos. of sodium thiosulphate is quickly poured in, followed at once by a solution of 4·8 kilos. of potassium dichromate in 75 litres of water. In order to complete the formation of the thiosulphonic acid the mixture is stirred for an hour. The whole is diluted to 600 litres and 6 kilos. of dimethylaniline hydrochloride are added. For the preparation of the indamine a saturated solution of 14 kilos. of potassium dichromate is now run in quickly at a temperature of 10°–12°, the whole being well stirred, 75 kilos. of a solution of zinc chloride (sp. gr. 1·53) added and the mixture heated for half an hour to 100°. On cooling the precipitated methylene blue is filtered off and purified by redissolving and precipitating with zinc chloride. (The amount of potassium dichromate added in the last operation is sufficient both to form the indamine and to oxidise the leuco-methylene blue produced.)

By using methylethylaniline instead of dimethylaniline a much greener dyestuff is obtained (*Methylene blue, M.E.* Cain, 7th Int. Cong. App. Chem. London, 1909, sect. iv. B, 95).

(For the preparation of methylene blue on the laboratory scale, *see* Cain and Thorpe, Synthetic Dyestuffs, 4th ed., 1918, 289; Möhlau and Bucherer, Farbenchemisches Praktikum, 1908, 262.)

Methylene blue may be estimated by titrating a boiling solution with titanous chloride in a current of carbon dioxide (Knecht, J. Soc. Dyers and Colourists, 1905, 21, 9).

Concentrated sulphuric acid dissolves methylene blue with a green colour. By reducing agents it is readily transformed into its leuco base, *tetramethyldiaminothiodiphenylamine*



This substance forms yellow needles, melting at 185° (Landauer and Weil, Ber. 1910, 43, 198); it rapidly oxidises on exposure to moist air, and is transformed into methylene blue.

Methylene blue is, with the exception of Victoria blue, the only basic blue colouring matter which has any technical importance, and it is preferable to Victoria blue on account of its greater fastness to light. It resists the action of neutral soaps and dilute solutions of chloride of lime. It is largely used in cotton-yarn dyeing and in calico-printing with tannin, or with tannin and tartar emetic mordants. It gives a greenish-blue inclining to indigo, and is frequently shaded with methyl violet, malachite green, and other basic colouring matters. It has no special applications in silk or wool dyeing. For pure blue cotton is mordanted with aluminium acetate, aged, passed through a chalk bath, well washed, passed through a weak tannin bath and dyed at a gradually increasing temperature. The colour is added in small portions to the dye-bath, which should not be warmer than 20°–25° at the beginning, and after some colour has been taken up it should be heated very gradually to 70°–80°, or higher if required; a small amount of acetic acid in the dye-bath acts favourably for level dyeing. For very dark indigo shades cotton, mordanted with tannin and antimony, may be passed through a weak solution of pyrolignite of iron; or a bath of pyrolignite of iron (6° Tw.) may be substituted for tartar emetic; after the treatment with iron liquor the cotton should be passed through weak lime water and finally well washed before dyeing (Knecht, Rawson and Loewenthal, A Manual of Dyeing, 2nd ed., 1910, 484). For method of detection on dyed fabrics, *v.* vol. ii. p. 592.

Methylene blue is of considerable value as a staining material in bacteriological and histological research; *v.* Ehrlich, Centralb. Medic. Wissensch. 1885; Dresser, Zeitsch. Biol. 1885, 41; A. B. Lee, The Microtomist's Vade-Mecum; J. W. H. Eyre, The Elements of Bacteriological Technique.

J. C. C.

METHYLENE GREEN. A substance obtained by treating methylene blue with nitrous acid, or with nitric acid in sulphuric or acetic acid solution. It is a mono-nitro derivative of methylene blue. The leuco compound forms brown needles melting at 146°–147°. It is applied to cotton in the same way as methylene blue, and gives a full bluish-green shade.

Literature.—Eng. Pat. 8992, 1886; D. R. P. 38979; Fr. Pat. 177331; Ber. 1906, 39, 1020; Z. Farben. Ind. 1906, 5, 285; J. pr. Chem. 1907, [ii.] 76, 401; Ber. 1910, 43, 198.

J. C. C.

METHYLENE VIOLET *v. Safranines*, art. AZINES.

METHYLETHYL ACETIC ACID *v.* VALERIC ACIDS.

METHYLETHYLALLOXAN *v.* ALLOXAN.

METHYLETHYLBENZENE *v.* CUMENES.

METHYLGLUCOSIDE *v.* CARBOHYDRATES.

METHYLGLYOXAL *v.* KETONES.

METHYLGRANATONINE *v.* KETONES.

METHYL GREEN *v.* TRIPHENYL METHANE COLOURING MATTERS.

METHYLHEXYL ACETIC ACID. NONOIC ACID (*q.v.*).

METHYLHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

METHYLINDENE *v.* INDENE.

METHYLINDOLES *v.* INDOLES.

METHYL*iso*PROPYLACETIC ACID *v.* CAPROIC ACIDS.

METHYL*iso*PROPYLPROPIONIC ACID *v.* HEPTOIC ACIDS.

METHYLMALIC ACID *v.* MALIC ACID.

METHYLNAPHTHALENES, THEIR HOMOLOGUES and DERIVATIVES. α- and β-methylnaphthalenes occur in creosote oil (Schulze, Ber. 1884, 17, 842, 1527), and, together with naphthalene and di-, tri-, and tetramethylnaphthalene, in crude petroleum or naphtha (Tammann, D. R. P. 95579, 1897). The separation of these substances from their homologues is effected either by fractional sulphonation or by distillation, and their purification by means of picric acid (Tammann, *l.c.*; Wichelhaus, Ber. 1891, 24, 3918; Wendt, J. pr. Chem. 1892, [ii.] 46, 319). The pure methylnaphthalenes were placed on the market in 1912 (Ges. f. Teerverwertung, m.b. H. Duisburg-Meiderich). α-*Methylnaphthalene*, colourless oil, b.p. 237°-241° or 117°-120° under 12-13 mm., forms a *picrate*, orange-yellow needles, m.p. 141°-142° (N.B. usually given in the literature as 116°-117° from Ciamician, Ber. 1878, 11, 272, whose compound was actually the picrate of β-methylnaphthalene). Sulphonation yields two isomeric *sulphonic acids*, separable by means of their barium salts (Wendt, *l.c.*). Contrary to the statement of Scherler (Ber. 1891, 24, 3932) the nitration of α-methylnaphthalene in the cold results in the formation of α-*methyl*-4-*nitronaphthalene*, yellow needles, m.p. 71°-72°, together with a mixture of liquid products, b.p. 173° 179° under 18 mm., which has not been satisfactorily separated (Lesser and Glaser, Annalen, 1913, 402, 1). Further nitration does not yield a dinitro-derivative, but a *trinitro*-derivative, straw-yellow needles, m.p. 180°-181° (*ibid.*). 4-*Methyl*-α-*naphthylamine*, colourless needles, m.p. 51°-52°, obtained by the reduction of the corresponding nitro-derivative, forms an *acetyl*-derivative, needles, m.p. 166°-167°, a *benzoyl*-derivative, needles, m.p. 238°-239°, and condenses normally with chlorodinitrobenzene to form the *dinitrophenyl*-derivative, yellow needles, m.p. 176°-177°, with picryl chloride to form the *trinitrophenyl*-derivative, scarlet-red prisms, m.p. 237°-238°, and with phthalic anhydride to form 4-*methyl*-α-*naphthylphthalimide*, colourless needles, m.p. 233°-234° (*ibid.*). The reduction of monoazo-derivatives of 4-methyl-α-naphthylamine yields 4-*methyl*-1 : 2-*naphthylene diamine*, colourless needles, m.p. 91°-92°, together with *dimethyldinaphthazine*, golden-yellow needles, m.p. 305°-306°; the former compound condenses with phenanthraquinone to form the *azine*, yellow needles, m.p. 341°-342° (*ibid.*). The azo dyes prepared from aminomethylnaphthalenes (Akt-G., D. R. P. 15647; Eng. Pat. 750, 1881) have no technical value. 1-*Methyl*-β-*naphthylamine*, needles, m.p. 51°, obtained by heating 1-methyl-β-naphthol with calcium chloride ammonia for 8 hours at 270°, forms an *acetyl*-derivative, needles, m.p. 189° (Fries and Hübner, Ber. 1906, 39, 435).

2-*Iodo*-1-*methylnaphthalene*, pearly leaflets, m.p. 51·5°, obtained from the corresponding amine by the diazo-reaction, is converted into 1′:1-*dimethyl*-2:2′-*dinaphthyl*, colourless needles, m.p. 230°, by heating with finely divided copper at 220°-260° (Scholl and Tritsch, Monatsh. 1918, 39, 231). By the action of phthalic anhydride and aluminium chloride on α-methylnaphthalene, 4′-*methyl*-α-*naphthoyl*-*benzoic acid*, m.p. 167°-169°, is formed which, when reduced with zinc and acetic acid, yields the *lactone* of ω-*hydroxy*-ω-4′-*methyl*-α-*naphthyl*-o-*toluic acid*, m.p. 163°-164°, but when reduced with zinc-dust and sodium hydroxide, yields ω-4′-*methyl*-α-*naphthyl*-o-*toluic acid*, m.p. 183°-184°; the ammonium salt of the latter compound on heating with sulphuric acid condenses to 5-*methyl*-1 : 2-*benzanthraquinone*, yellow needles, m.p. 176°-177°, and this undergoes oxidation and condensation when heated with alkali, with formation of 1 : 2 : 1′ : 2′-*dibenzanthraflavone*, orange-red crystals, which dyes cotton yellow from an alkaline hydrosulphite vat (Scholl and Tritsch, Monatsh. 1911, 32, 997). 1-Methyl-β-naphthyl amine, its acetyl- or phthaloyl-derivatives do not condense with phthalic anhydride (Scholl and Tritsch, Monatsh. 1912, 33, 307). Diazotisation of 4-methyl-α-naphthylamine followed by the usual treatment yields 4-*methyl*-α-*naphthol*, colourless needles, m.p. 84°-85°, which forms a *benzoyl*-derivative, large prisms, m.p. 81°-82° (Lesser and Glaser, *l.c.*). Reduction of dinaphtholmethane with zinc dust and sodium hydroxide gives a 90 p.c yield of 1-*methyl*-β-*naphthol*, white needles, m.p. 112°, which forms a *benzoyl*-derivative, needles, m.p. 117°; *ethyl ether*, plates, m.p. 52° (Meister, Lucius and Bruning, D. R. P. 161450, 1904); *methyl ether*, plates, m.p. 39°; *acetyl*-derivative, prisms, m.p. 66°; 6-*bromo*-1-*methyl*-β-*naphthol*, needles, m.p. 129°; 3 : 6-*dibromo*-1-*methyl*-β-*naphthol*, needles, m.p. 180° (Fries and Hübner, *l.c.*). 1-Methyl-β-naphthol does not couple with diazo-compounds. Nitrous acid converts 1-methyl-β-naphthol into 1 : 2-*methylnaphthaquinonitrole*, colourless needles, m.p. 60°, which, when heated with acetic acid and ether, yields 1 : 2-*methylnaphtha*-ψ-*quinol*, colourless plates, m.p. 89°; 6-*bromo*-1 : 2-*methylnaphthaquinonitrole*, needles, m.p. 99° (decomp.); 6-*bromo*-1 : 2-*methylnaphtha*-ψ-*quinol*, yellow plates, m.p. 84°: 6-*bromo*-3-*nitro*-1 : 2-*methylnaphtha*-ψ-*quinol*, golden-yellow plates, m.p. 155°, is reduced by sulphurous acid to 6-*bromo*-3-*nitro*-1-*methyl*-β-*naphthol*, orange-red needles, m.p. 163°, but reduction with zinc-dust and hydrochloric acid yields 6-*bromo*-3-*amino*-1-*methyl*-β-*naphthol*, colourless needles, m.p. 163°, which forms a *monoacetyl*-derivative, needles, m.p. 183°, and a *diacetyl*-derivative, needles, m.p. 240° (*ibid.*). By the use, alternately, of chlorine, sodium acetate and acetic acid, 1-methyl-β-naphthol is converted into 1 : 3 : 4-*trichloro*-2-*keto*-1-*methyltetrahydronaphthalene*, m.p. 78°; 1 : 3-*dichloro*-2-*keto*-1-*methyldihydronaphthalene*, oil; 1 : 3 : 3 : 4-*tetrachloro*-2-*keto*-1-*methyltetrahydronaphthalene*, m.p. 124°-125°; 1 : 3 : 4-*trichloro*-2-*keto*-1-*methyldihydronaphthalene*, m.p. 85°, and 1 : 3 : 3 :

4 : 4-*pentachloro-2-keto-1-methyltetrahydronaphthalene*, m.p. 105° (Fries and Hempelmann, Ber. 1908, 41, 2614). The reduction of 1 : 3-dichloro-2-keto-1-methyldihydronaphthalene with stannous chloride yields 3-*chloro-1-methyl-β-naphthol*, needles or scales, m.p. 60°, 1 : 3 : 4-trichloro-2-keto-1-methyldihydronaphthalene similarly yields 3 : 4-*dichloro-1-methyl-β-naphthol*, needles, m.p. 132° (*ibid.*). When chlorine is passed into a solution of 1-methyl-β-naphthol in slightly diluted acetic acid at 0°, 1-*chloro-2-keto-1-methyl-β-naphthol* is ultimately obtained as a colourless oil (*ibid.*), which, when saturated with chlorine and heated in a closed vessel on the water-bath for 5 hours, is converted into 4-*chloro-1-methyl-β-naphthol*, white needles, m.p. 101° (Fries, Ber. 1921, 54, 2925). Treatment of 6-bromo-1 : 2-methyl-naphtha-ψ-quinol with acetyl chloride, followed by saponification, yields 1-*methyl-4-chloro-6-bromo-β-naphthol*, white needles, m.p. 179° (*ibid.*). *Dehydro-1-methyl-β-naphthol*, yellow prisms, m.p. 133°–134°, is formed by the oxidation of 1-methyl-β-naphthol with alkaline ferricyanide (Pummerer and Cherbuliez, Ber. 1914, 47, 2957) or with nitrous acid (Fries and Hubner, *l.c.*).

β-Methylnaphthalene, monoclinic prisms, m.p. 32·5°, b.p. 240°-242° (Fock, Ber. 1894, 27, 1247), forms a *picrate*, needles, m.p. 115° (Schulze, *l.c.*). Sulphonation yields two isomeric *sulphonic acids* separable by means of their barium salts (Wendt, *l.c.*), and nitration yields 1-*nitro-β-methylnaphthalene*, m.p. 81°, b.p. 185°-186° under 18 mm., which forms a *monobromo*-derivative, needles, m.p. 94° (Schulze, *l.c.*; Lesser and Aczél, Annalen, 1913, 402, 30). The reduction of 1-*nitro-β-methylnaphthalene* with acid stannous chloride yields 4-*chloro-2-methyl-α-naphthylamine*, colourless needles, m p. 65°; *acetyl*-derivative, needles, m.p 206°; *benzoyl*-derivative, needles, m.p. 236°–237°; the chlorinated base condenses with phthalic anhydride to form 4-*chloro-2-methyl-α-naphthylphthalimide*, colourless needles, m.p. 171°, but it reacts additively with chlorodinitrobenzene and picryl chloride forming red needles, m p. 78°, and brownish-red needles, m.p. 119°, respectively (Lesser and Aczél, *l.c.*). The reduction of 1-nitro-β-methylnaphthalene with iron and acetic acid yields 2-*methyl-α-naphthylamine*, colourless needles, m.p. 32°; *acetyl*-derivative, needles, m.p. 188°; *benzoyl*-derivative, plates, m.p. 180°; the base condenses with phthalic anhydride to form 2-*methyl-α-naphthylphthalimide*, colourless needles, m.p. 233°–234°, but it reacts additively with chlorodinitrobenzene and picryl chloride forming red needles, m.p. 93°–94°, and brownish-red needles, m.p. 129°–130°, respectively (*ibid.*). Reduction of an alcoholic solution of 1-nitro-β-methylnaphthalene with tin and hydrochloric acid does not give the chloro-derivative but 2-methyl-α-naphthylamine, which on chlorination yields a *tetrachloro*-derivative of 2-*methyltetrahydro-α-naphthaquinone*, colourless prismatic crystals, m.p 118°; on reduction the latter yields 4-*chloro-2-methyl-α-naphthol*, colourless needles, m.p. 104·5°; *acetyl*-derivative, needles, m.p. 87°; 2-*methyl-α-naphthaquinone*, yellow needles, m.p. 104°; 4 : 4′-*diamino-3* : 3′-*dimethyldinaphthyl*, colourless prisms, m.p. 213° (Fries and Lohmann, Ber. 1921, 54, 2912). 2-*Methyl-α-naphthol*, colourless needles, m.p 61°, is obtained from the corresponding amine by the diazo-reaction, the decomposition being effected in an atmosphere of carbon dioxide, and 4 : 4′-*dihydroxy-3* : 3′-*dimethyl-1* : 1′-*dinaphthyl*, large plates, m.p. 235° (decomp.), is formed as a by-product; the latter compound forms a *diacetyl*-derivative, plates, m.p. 235°–236°, and readily oxidises, as also does 2-methyl-α-naphthol, to 2 : 2′-*dimethyl-1* : 1′-*dinaphthone*, metallic needles with a green reflex and carmine-red streak, decomp. about 250° (Lesser and Aczél, *l.c.*).

Naphthylalkyl ketones are converted quantitatively into the corresponding hydrocarbons by direct hydrogenation at 180° in the presence of nickel (Darzens and Rost, Compt. rend. 1908, 146, 933), thus α- and β-ethylnaphthalenes from the corresponding acetylnaphthalenes, and α- and β-isobutylnaphthalenes from the corresponding isobutyrylnaphthalenes.

α-Ethylnaphthalene, does not set at −18°, b.p. 100° under 2–3 mm (*ibid.*), forms a *picrate*, yellow needles, m.p. 98° (Carnelutti, Ber. 1880, 13, 1672), and a *monosulphonic acid* (Fittig and Remsen, Annalen, 1870, 155, 118).

β-Ethylnaphthalene, crystallises at −18°, b.p. 250°–251° (Marchetti, Gazz. 11, 265, 439; Brunel, Ber. 1884, 17, 1179), forms a *picrate*, golden-yellow needles, m.p. 69° (Brunel), 71° (Marchetti), and a *monosulphonic acid* (*ibid.*).

α-iso-Butylnaphthalene, mobile liquid with an odour of petroleum, b.p. 136°–138° under 11 mm. (Darzens and Rost, *l.c.*).

β-iso-Butylnaphthalene, mobile liquid with a faint odour, b.p. 112°-113° under 6 mm. (*ibid.*).

1-*Allyl-β-naphthol*, obtained by heating β-naphthol allyl ether at 210° until soluble in dilute sodium hydroxide, forms colourless prisms, m.p. 55°, b.p. 177°–178° under 12 mm.; *benzoate*, colourless crystals, m p. 65° (Claisen, D. R. P. 268099, 1912; Ber. 1912, 45, 3157; Claisen and Eisleb, Annalen, 1913, 401, 61).

2-*Allyl-α-naphthol*, is not formed so readily as its isomeride, oil, b.p. 171° under 12 mm.; *p-nitrobenzoate*, needles, m.p. 99° (*ibid.*). The reaction by which these derivatives of allylnaphthalene are formed is not applicable to other ethers.

Dimethylnaphthalenes.

1 : 4-*Dimethylnaphthalene*, obtained by the action of methyl iodide and sodium on 1 : 4-dibromonaphthalene (Mono, Ber. 1880, 13, 1517), does not set at −18°, b.p. 262°–264° under 751 mm., forms a *picrate*, orange needles, m.p. 139° (Giovannozzi, Gazz. 12, 147) or 141° (Cannizzaro and Andreocci, Gazz. 26, 19), and a *monosulphonic acid* (Giovannozzi). Physical methods for the separation of the dimethylnaphthalenes in the heavy-oil fraction of coal tar, b.p. 160°–265°, are inapplicable, but the sulphonation method under varying conditions leads to the isolation of 1 : 6-, 2 : 6-, and 2 : 7-dimethylnaphthalenes.

1 : 6-*Dimethylnaphthalene*. The crude oil, purified by alternate fractionation and agitation with small quantities of cold sulphuric acid, is stirred with 60 p.c. of its weight of 98 p.c. sulphuric acid for 8–10 hours at 40°. The pasty mass of sulphonic acids which separates is mixed with a little water when a solid sulphonic acid is deposited. The latter is crystallised from 33 p.c. sulphuric acid and

hydrolysed by steam at 130°–140° to 1 : 6-*dimethylnaphthalene*, b.p. 262°–263°, which forms a *picrate*, orange-red needles, m.p. 114° ; 1 : 6-*dimethylnaphthalene-4-sulphonic acid* forms a *sodium salt*, bundles of needles, $1H_2O$, and an *amide*, prismatic crystals, m.p. 185° ; alkaline fusion of the sulphonic acid yields 4 : 7-*dimethyl-α-naphthol*, needles, m.p. 82° ; 2 : 5-*dimethyl-α-naphthaquinone*, pungent smelling yellow needles, m.p 95° (Weissgerber and Kruber, Ber. 1919, 52, 346).

2 : 6-*Dimethylnaphthalene.* When sulphonation is effected at 135°–140° and the product poured on to ice, a much less soluble sulphonic acid separates and is crystallised from 20 p.c. sulphuric acid. Hydrolysis yields 2 : 6-*dimethylnaphthalene*, m.p. 110°–111°, b.p. 261°–262°, which forms a *picrate*, orange-yellow needles, m.p. 142°–143° (*ibid.* ; Baeyer and Villiger, Ber. 1899, 32, 2443). Sulphonation in the cold yields the freely soluble 2 : 6-*dimethylnaphthalene-8-sulphonic acid*, flat needles and tablets, *sulphonic chloride*, prisms, m.p. 105°–107° ; *amide*, leaflets, m.p. 207° ; alkaline fusion yields 3 : 7-*dimethyl-α-naphthol*, needles, m.p. 105°–106° (Weissgerber and Kruber, *l.c.*). Sulphonation at 135°–140° yields 2 : 6-*dimethylnaphthalene 7-sulphonic acid*, which is also formed by heating the isomeride with 78 p.c. sulphuric acid at 135°–140° ; *sodium salt*, glistening plates, $5H_2O$; *amide*, needles, m.p. 265°–266° ; alkaline fusion yields 3 : 7-*dimethyl-β-naphthol*, needles, m.p. 173°–174° ; 2 : 6-*dimethyl-α-naphthaquinone*, yellow needles, m.p. 136°–137° ; 3 : 7-*dimethyl-β-naphthaquinone*, ruby-red needles, m.p. 151°–152° (*ibid.*).

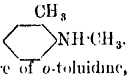
2 : 7-*Dimethylnaphthalene.* After 1 : 6-dimethylnaphthalene sulphonic acid has been removed from the cold sulphonation mixture, the liquid sulphonic acids are heated to 150°–160° for a few hours and hydrolysed. The mixture of solid and liquid hydrocarbons formed may be sufficiently rich in the 2 : 6-isomeride to allow it to be separated by fractional crystallisation, but, if not, it is sulphonated at 135°–140° and the solid 2 : 6-dimethylnaphthalene sulphonic acid removed. The residue is hydrolysed, the hydrocarbons sulphonated with 98 p c. sulphuric acid for 2–3 hours at 40°, and the pasty product after crystallisation from 2–3 parts of 30 p.c. sulphuric acid, is hydrolysed. 2 : 7-*Dimethylnaphthalene*, glistening leaflets, m.p. 96°–97°, b.p. 262°, forms a *picrate*, yellow needles, m.p. 135°–138° ; sulphonation at 100° yields 2 : 7-*dimethylnaphthalene-3-sulphonic acid*, pearly sword-like crystals ; *sodium salt*, needles ; *amide*, needles, m.p 197°–198° ; alkaline fusion yields 3 : 6-*dimethyl-β-naphthol*, lanceolate crystals, m.p. 171°–172° ; 3 : 6-*dimethyl-α-naphthaquinone*, yellow needles, m.p. 114°–115° ; 3 : 6-*dimethyl-β-naphthaquinone*, brownish-red prisms, m.p. 152°–153° (*ibid.*).

2 : 3-*Dimethylnaphthalene*, leaflets, m.p. 104°–105°, b.p. 139°–140° under 15 mm., obtained by the hydrolysis of a sulphonic acid accidentally isolated from the liquid sulphonic acids accompanying 2 : 6-dimethylnaphthalene sulphonic acid (Weissgerber, Ber. 1919, 52, 370), is identical with *guaiene*, obtained by the dry distillation of guaiacum resin (Schroeter, Lichtenstadt and Ireneu, Ber 1918, 51, 1587); *picrate*, m.p. 129·5°–130·5°.

The coal tar fraction, b.p. 220°–290°, is often used as a solvent for other fractions, yet the only genuine oils which it contains are β-methylnaphthalene and 1 : 6-dimethylnaphthalene, and it owes its fluidity to the enormous depression of the freezing point mutually exerted by the ingredients. Naphthalene might well find an outlet as an oil, therefore, if it were methylated. F. M. R.

METHYL ORANGE *v.* Azo- colouring matters.

METHYL-*o*-TOLUIDINE



Prepared by heating a mixture of *o*-toluidine, methyl alcohol and hydrochloric acid, or a mixture of *o*-toluidine, methyl alcohol and iodine. B.p. 207°–208°; sp gr. 0·973 at 15°.

METHYLPHENYL HYDRAZINE-HYDRAZONES *v.* Hydrazines and Hydrazones.

METHYLPSYCHOTRINE *v.* Ipecacuanha.

2-METHYLQUINOLINE-QUINALDINE *v.* Quinoline.

METHYLRHODIN. Trade name for methyl acetyl salicylate.

METHYL VIOLET *v.* Triphenyl methane colouring matters.

METOL. Trade name for methyl-*p*-aminophenol sulphate. Used as a photographic developer. Obtained by heating quinol with aqueous methylamine under pressure and pouring the product into sulphuric acid (Merck. D. R. P. 260234; *cf.* Harger, J. Amer. Chem. Soc. 1919, 41, 270). M.p. 250°–260° (decomp.). Soluble in 6 parts boiling water and 20 parts of water at 25°. Gives an intense purple coloration with mercuric acetate.

METOQUINONE. Trade name for a photographic developer obtained by the action of methyl-*p*-aminophenol sulphate (metol) on hydroquinone (quinol).

METRAMINE. Syn. for hexamethylenetetramine.

METTERNICH GREEN. A double salt of zinc chloride with the chlormethyl-hexamethyl rosaniline hydrochloride. Known also as *iodine green* or *night green.* Obtained by the action of methyl iodide or chloride upon rosaniline (Hofmann and Girard, Ber. 2, 442 ; Appenzeller, *ibid.* 6, 965).

MEXICAN BUCKEYE OIL. An oil extracted from the seeds of *Ungnadia speciosa* (Endl.), a deciduous shrub belonging to the family *Sapindaceæ*, found in Texas, New Mexico, &c. Pale yellow ; sp. gr. 0·912 at 15° ; m.p. −12°. Saponification value, 191–192 ; iodine value, 81–82 ; Hehner value, 94 ; iodine value of fatty acids, 86–87 (Schaedler Pharm. Zeit. 1889, 340). Similar values have been obtained by Cheel and Penfold from an Australian-grown plant (J. Soc. Chem. Ind. 1919, 74 T.). The seeds contain a cyanogenetic glucoside which may militate against its use as a salad oil for which it is otherwise suitable.

MEZCALINE AND THE ALKALOIDS OF ANHALONIUM SPP.—In Mexico Cactaceæ, belonging to the genus *Anhalonium*, notably *A. Lewinii* (Hennings), are used in Indian religious ceremonies as narcotics, under the name ‘pellote.’ The dried flowering heads of *A. Lewinii* are known as ‘mescal buttons,’ and contain (Heffter, Ber. 1896, 29, 216) mezcaline 6·3 p.c., anhalonidine 5·3 p.c., anhalonine 3 p.c., and lophophorine 0·5 p.c. The constitution of most of these has been established by Späth (Monatsh. 1919, 40, 129; 1921, 42, 263), and as far as is known they may be divided into substituted phenylethylamines and tetrahydroisoquinolines, derived therefrom by condensation with aldehydes. They supply an illustration of the way in which alkaloids may be derived from protein aminoacids.

Anhaline $C_{10}H_{15}O_3N$ occurs in *A. fissuratum* (Engrlm.), and is identical with hordenine, *q.v.*

Mezcaline $C_{11}H_{17}O_3N$, a syrup, the chief alkaloid of 'mescal buttons,' is β-3·4:5-trimethoxyphenylethylamine and has been synthesised by Spath.

The other series of bases are derivatives of 6:7:8-trihydroxytetrahydroisoquinoline.

Anhalamine $C_{11}H_{15}O_3N$, m.p. 185·5°, is the dimethyl ether of the above; the position of the free phenolic group remains undetermined. Its methyl ether is readily synthesised from mezcaline and formaldehyde. Anhalonidine and pellotine seem to be formed in the plant by similar condensations with acetaldehyde and both contain a methyl group in position 1. Both are optically inactive.

Anhalonidine $C_{12}H_{17}O_3N$, m.p. 154°, is the dimethyl ether of 1-methyl-6:7:8-trihydroxytetrahydroisoquinoline and a homologue of anhalamine.

Pellotine $3_{13}H_{19}O_3N$, m.p. 110°, occurs in *A. Williamsii* (Lem.) and in *A. Lewinii* (Hennings), and is a still higher homologue containing a methyl group attached to nitrogen. It is almost certainly a dimethyl ether of 1:2-dimethyl-6:7:8-trihydroxytetrahydroquinoline. Complete methylation of the last two bases results in the same quaternary iodide of a trimethylether. The other alkaloids from *A. Lewinii* have been described by Heffter, but have not been closely investigated by Spath. They both contain only one methoxy group.

Anhalonine $C_{12}H_{15}O_3N$, needles, m.p. 85°, is a secondary base.

Lophophorine $C_{13}H_{17}O_3N$, is a syrup, yielding crystalline salts. These two alkaloids are doubtless very closely related to the better known ones of the cyclic (second) group.

According to Dixon (Zeitsch. Physiol. 1899, 25, 69; *cf.*, also Mogilewa, Arch. expt. Path. Pharm. 1903, 49, 137), anhalonidine, anhalonine, lophophorine, and mezcaline exert qualitatively the same physiological action, lophophorine being the most powerful and mezcaline the most active in producing colour visions. In man the alkaloids produce first excitement and then intoxication, resembling that caused by alcohol but accompanied by a number of subjective sensations including colour visions and a feeling of dual existence. Pellotine has occasionally been employed in medicine as a narcotic. Older papers on the subject are by Lewin (Arch. expt. Path. Pharm. 1888, 24, 401; 1898, 34, 374), and by Heffter (Ber. 1894, 27, 2975; 1896, 29, 216; 1898, 31, 1193). G. B.

MIARGYRITE. Silver sulphantimonite $AgSbS_2$, occurring as small, usually indistinct, monoclinic crystals. These are black and opaque, with a metallic lustre, but thin splinters transmit a deep crimson colour; streak dark cherry-red; sp. gr. 5·2. Crystals were formerly found at Bräunsdorf, near Freiberg in Saxony, and compact masses of some size are met with in the silver mines of Bolivia. L. J. S.

MICA (Ger. *Glimmer*). A name applied to a group of minerals characterised by the facility with which they split into thin laminæ, which are flexible and more or less elastic. It is now believed that all micas belong to the monoclinic system, but the crystals often affect a hexagonal habit. The perfect cleavage, on which the micaceous structure depends, is parallel to the basal plane. A similar structure is seen in the group of chlorites, but their laminæ, though flexible, are not elastic. The hardness of the micas is between 2 and 3; while their sp.gr. ranges from 2·7 to 3·1. The optical characters and chemical composition are subject to considerable variation in different species. Broadly speaking, there is a group of potash-micas, generally of pale colour, and having the optic axes separated by wide angles; and a group of magnesian, or ferro-magnesian, micas, usually of dark colour, with the optic axes in some cases so close that the mineral becomes apparently uniaxial. On sharply striking a plate of mica with a needle-point, a six-rayed star is produced (*percussion-figure*); while pressure with a blunt instrument develops a similar figure (*pressure-figure*), having each ray at right angles to one in the percussion-figure.

All the micas are complex silicates, containing aluminium and potassium, generally with magnesium, but rarely with calcium. The potassium is frequently replaced in part by lithium and sodium, while iron may be substituted for the magnesium and aluminium. Water is always present, and many micas contain fluorine. The chemical constitution of the group of micas has been discussed by Rammelsberg (Min. Chem.) and by Tschermak (Zeitsch. Kryst. 1878, 2, 14; 1879, 3, 122), and later by F. W. Clarke (Amer. Chem. J. 1889, 38, 384; Bull. United States Geol. Survey, 1895, No. 125: 1914, No. 588). The following analysis will serve to illustrate the composition of the principal species:—

	I.	II.	III.	IV.
SiO_2 . .	45·05	50·98	41·68	39·30
Al_2O_3 . .	30·57	27·80	13·21	16·95
Fe_2O_3 . .	1·14	—	0·16	0·48
FeO . .	1·73	0·05	0·11	8·45
CaO . .	—	—	—	0·82
MgO . .	0·97	—	28·16	21·89
K_2O . .	10·23	10·78	8·78	7·79
Na_2O . .	2·13	—	1·04	0·49
Li_2O . .	—	5.88	—	—
H_2O . .	6·19	0·96	3·10	4·02
F. . .	1·26	7·88	3·07	0·89
	99·27	104·38	101·77	101·08
Sp.gr. . .	2·80	2 84	2·86	2·86

I, Muscovite from Haddam, Connecticut (Schlaepfer, 1891). II, Lepidolite from Rozena, Moravia (F. Berwerth quoted by G. Tschermak, 1878; also P_2O_5 0·05). III, Phlogopite from De Kalb, New York (S. L. Penfield, 1892; also TiO_2 0·38, BaO 2·08. IV, Biotite from Vesuvius (F. Berwerth, 1877).

Muscovite, or potash-mica $H_2KAl_3(SiO_4)_3$, is the common species widely distributed as a constituent of granite, gneiss, and mica-schist. It is usually white, grey, or yellow; and the angle of the optic axes may be as much as 70°. Some forms of muscovite have been mistaken for talc, as in the granitic rock of the Alps called protogine, and in certain so-called talc-schists. *Sericite* is a silky talc-like mica, occurring in the schists of the Taunus. A rare variety of muscovite containing 6 p.c. of baryta has been called *oellacherite* or baryta-mica. *Fuchsite*, or chrome-mica, of a bright-green colour, is a variety containing about 4 p.c. of chromic oxide. The *paragonite* of St. Gotthard, closely related to muscovite, is a soda-mica $H_2NaAl_3(SiO_4)_3$.

Lepidolite, or lithia-mica, with the approximate formula $KLi[Al(OH,F)_2]Al(SiO_3)_2$, is generally of peach-blossom colour, but sometimes grey or white, with a pearly lustre. It occurs in certain granites, especially with minerals containing fluorine, like topaz and tourmaline. Small amounts of rubidium and cæsium are sometimes present in lepidolite. The best-known locality for the typical kind is near Rozena in Moravia, where it forms a beautiful rock, occasionally polished as an ornamental stone. During recent years lepidolite has been extensively mined at Pala in California for the supply of lithium salts largely used in the manufacture of lithia-water. *Zinnwaldite* is a greyish lithia-bearing mica, occurring in the tin-mining districts of Saxony, Bohemia, and Cornwall.

Phlogopite $[H,K,(MgF)]_3Mg_3Al(SiO_4)_3$ includes certain magnesian micas, usually of reddish or bronze colour, occurring in crystalline limestone and in serpentine. The angle of the optic axes ranges from 0° to 17°. It is notable that certain phlogopites exhibit by transmitted light luminous stars, due to the presence of multitudes of included acicular crystals definitely orientated; the best examples of this asteriated mica being yielded by some of the Laurentian limestones of Canada. The mica mined in Canada and Ceylon for commercial purposes is phlogopite.

Biotite includes a number of magnesian and ferro-magnesian micas, generally of dark colour, and transparent only in thin laminæ. Frequently occurring in six-sided plates, and having a very small optic angle, they were formerly referred to the hexagonal system. In thin sections they exhibit strong pleochroism. They are generally denser than muscovite, and their cleavage-laminæ are less elastic. Biotite is often found, in association with muscovite, in granite, gneiss, and mica-schist, and the two micas are sometimes closely intergrown. The biotitic micas also occur in mica-syenite, mica-porphyry, and trachyte; while sharply developed crystals are not uncommon in the ejected blocks of Monte Somma. The Vesuvian dark micas were termed by Breithaupt *meroxene*, and this name has been revived by Tschermak for all the true biotites, while he uses the term *anomite* to distinguish a similar mica, differing only in optical characters. *Rubellane*, an opaque red mica from certain volcanic rocks, is merely an altered biotite, which has lost its elasticity. In *lepidomelane*, the aluminium of an ordinary biotite is largely replaced by iron, and the mica becomes black and is attracted by a powerful magnet. Heddle's *haughtonite* of the Scottish granites, differs from biotite by containing less magnesium, and from lepidomelane by having most of its iron in the condition of FeO, the average percentage of this oxide being 17·22.

The vanadium-mica, or *roscoelite*, occurring with gold ores in California and Colorado, contains as much as 28·85 p.c. V_2O_3. *Margarite*, or lime-mica, $H_2CaAl_4Si_2O_{12}$ is sometimes placed in the mica group, though more usually it is classified with the clintonites or 'brittle micas.'

The mica of commerce comes mostly from India, the United States, and Canada; the Canadian being the brownish magnesian mica phlogopite, known in the trade as 'amber.' Large sheets of sufficient purity to be profitably worked are of very limited occurrence; they are usually found in veins of pegmatite or giant granite, where the constituents crystallise on a large scale, and are often associated with rare minerals such as beryl and columbite. In India the chief mica-mining districts are those of Hazáribágh in Bengal and of Nellore in Madras; from the former the mica (muscovite) is usually of a pale ruby tint, and from the latter of a greenish shade. In the Inikúrti mine, Nellore, 'books' of mica measuring 10 feet across the basal plane and up to 15 feet across the folia have been found. Rectangular sheets measuring 30 × 24 inches and free from flaws have frequently been obtained. A single mica crystal from North Carolina has been known to weigh nearly 2000 pounds. Mica has been worked at Alstead, in New Hampshire, where sheets have been found measuring 4 feet across. Mining for mica has also been carried on in the Black Hills of South Dakota, in Virginia, and in New Mexico. Several mines have now been opened up in the Uluguru Mountains, in Tanganyika Territory.

Of the various micas, muscovite and phlogopite are the only ones of commercial importance; and these, strangely enough, often pass in trade under the name of 'talc.' Muscovite was formerly called 'Muscovy glass,' in allusion to its use in Russia as a substitute for window-glass. At the present day it is employed as a transparent fire-resisting medium in the doors of stoves and furnaces, and for lamp-shades and gas-covers. It is also used for the dial-plates of compasses, while in the East, especially in India, it is applied to various ornamental purposes. Paintings on mica, executed by native artists, are well known to collectors. Sheets of mica, used as a decorative material, have been found in the prehistoric mounds of the Mississippi Valley.

Many other practical uses of mica might be mentioned. Its most extensive application at the present day depends on the fact that it is a bad conductor of electricity. The smooth, flexible sheets are used in the construction of the armatures of dynamos and in other parts of electrical machinery and instruments. Extensive use is also made for insulating purposes of a manufactured material known as *micanite* or *micanite cloth*. This consists of scraps of mica cemented by shellac on to cloth or paper.

The preparation of mica for the market is very simple. The blocks of rough mica, having been freed from associated minerals, or dressed, are split into plates, which are then 'scribed,' or marked out into patterns, and along this scribing the mineral is cut by means of shears. A good deal of refuse is necessarily produced.

This mica-waste is ground and used as a lubricating agent, and as an absorbent for nitroglycerin in the preparation of certain explosives; it has also been employed in the ornamentation of wall-papers, and to a limited extent as a substitute for asbestos.

References.—T. H. Holland, The Mica Deposits of India (Mem. Geol. Survey, India, 1902, 34, 11–121). The Mining and Preparation of Mica for Commercial Purposes (Bull. Imperial Institute, 1904, ii. 278–291). F. Cirkel, Mica, its Occurrence, Exploitation, and Uses (Mines Branch, Ottawa, 1905, 148 pp.; 2nd ed. by H. S. de Schmid, 1912, publ. No. 118, 411 pp. with 39 pls. and 22 maps). G. P. Merrill, The Non-metallic Minerals, 2nd ed. 1910. G. W. Colles, Mica and the Mica Industry, Philadelphia, 1906. Mica. Imp. Mineral Resources Bur., London, 1922. L. J. S.

MICHLER'S KETONE. Tetramethyldiaminobenzophenone (*q.v.*), art. Ketones.

MICROCIDIN. The sodium salt of β-naphthol used as an antiseptic.

MICROCLINE *v.* Felspar.

MICROCOSMIC SALT. *Ammonium sodium hydrogen phosphate* $NH_4{\cdot}NaHPO_4,4H_2O$, used as a flux in blowpipe tests.

MICROLITE. Pyro-tantalate (and columbate) of calcium (sodium, &c.), approximating in composition to $3Ca_2Ta_2O_7,NaF$. The mineral crystallises as regular octahedra, often minute in size, hence the name. They are yellow to brown with a resinous lustre, and transparent to opaque. Sp.gr. 5·2–5·6, H. 5½. The mineral is not attacked by hydrochloric acid, but is slowly decomposed by sulphuric acid. It is of rare occurrence in granitic and syenitic pegmatites, and has been found at Chesterfield in Massachusetts, in the mica mines at Amelia Court House in Virginia (here as good crystals an inch across and as rough crystals up to 4 lbs in weight), Uto in Sweden, Julianehaab district in South Greenland, Elba, Madagascar, and Western Australia. L. J. S.

MICROSOL. Trade name for an antiseptic made by mixing a solution of crude sulphophenolic acid with copper carbonate.

MIDDLETONITE *v.* Resins.

MIEMITE. A dolomite of an asparagus-green colour found in Tuscany, *v.* Dolomite.

MIERSITE *v.* Jodyrite.

MIGRALGINE. Trade name for a mixture of antipyrine 88 parts, caffeine 9 parts, and salicylic acid 3 parts, fused together.

MIGROL. A compound of pyrocatechin and pyramidone.

MIKADO ORANGE, -YELLOW *v.* Azo-colouring matters.

MILK. Milk is the term usually restricted to the liquid secreted by the mammary glands of the class of animals called mammalia. Certain secretions, however, which are produced by birds and by some species of plants more or less resemble ordinary milk in their general physical and chemical characters.

Milk is generally white in colour, with a faint yellow or bluish tinge. The yellow colour is due partly to lactochrome (probably identical with urochrome) and partly to the milk-fat which contains yellow pigments accompanying chlorophyll in all green plants; of these, xanthophyll, and more especially carotin are the most important; fresh green grass contains most and gives the highest coloured milk-fat (Palmer and Eckles, J. Biol. Chem. 1914, 17, 191). The white colour of milk is probably due to the peptisation of calcium phosphate by colloids. Milk is homogeneous and opaque, the opacity being due to particles of fat (milk globules) and to casein, the characteristic protein of milk, which in combination with lime and calcium phosphate exists in pseudo solution. When fresh it has a characteristic aroma. Immediately after drawing, it has in addition a faint odour of an exhalation from the skin which disappears on exposure to the atmosphere. The sp. gr. of milk in general varies between 1·018 and 1·045 (Scherer); that of human milk averages 1·032 (Simon), 1·03267 (1·02561–1·04648) (Vernois and Becquerel), 1·0313 (1·0353–1·0260) (Leeds, Chem. News, 50, 263); that of cow's milk varies between 1·029 and 1·033 (Bouchardat and Quevenne). The average of English cows' milk is 1·0322 (Vieth), of German cows 1·031 (Fleischmann). The sp. gr. of freshly drawn milk gradually increases on standing, due probably to some change in the physical state of the fat (*v. infra*).

The specific heat of milk is 0·96, varying slightly according to the percentage of fat (Richmond) and 0·9457 (Fleischmann, J. Landw. 1902, 50, 33), and it attains its maximum density between 0° and 1° (Fleischmann, L. V. S.[1] 17, 251). The refractive index of cow's milk was found by Valentin (Pfl. Arch. 1879, 78) to average 1·35 with Abbe's refractometer. The refractive index of human milk varies from 1·3475 to 1·3494, maximum 1·3518. Jorgenssen (L. J. 11, 699) found the refractive index of 23 samples of milk to vary from 1·347 to 1·3515; on the other hand, 29 samples of whey gave indices varying from 1·3465 to 1·3433.

The freezing-point of milk is −0·54° to −0·58° mean −0·554° (Beckmann, Milch. Zeit. 23, 702; Lajoux, J. Pharm. Chim. 1905, 577), −0·556° to −0·574° (Hamburger, Rec. trav. chim. 1896, 349); −0·55° to −0·57° (Winter, Compt. rend. 1895, 121, 696); −0·55° to −0·59° (Carlinfanti, Gazz. chim. ital. 1897, 460); −0·55° ±0·03° (Atkins, Chem. News, 1908, 97, 241); −0·545° to −0·565° (average −0·550°) (Maclaurin); −0·529° to −0·577° (Leather). In the case of a milk freezing at −0·555, the addition of 5 p.c. and 10 p.c. of water raised the freezing-point to −0·519° and −0·490° respectively. The average freezing-point of 141 samples of genuine milk was found by Monier-Williams to be −0·534° ±0·002° (corr.)—the values ranging from −0·558° to −0·514° (corr.).

The viscosity of milk depends upon the temperature, but the diminution in viscosity with rise of temperature is much more rapid in milk than in water. For the electrical conductivity of milk *v.* Coste and Shelbourn, Analyst, 1919, 158.

The reaction with litmus varies according to the species. Human milk is normally alkaline, whilst that of the carnivora is generally acid. Cow's milk, in common with all liquids containing both neutral and acid phosphate, in solution, is amphoteric—*i.e.* it will exhibit both acid and alkaline reactions. It is alkaline to methyl orange, amphoteric towards litmus and acid to phenolphthalein With the recognition of the facts that litmus is an acid of appreciable strength, and that the change of colour is due to a setting up of equilibrium between the bases combined with the phosphoric acid and litmus respectively, the amphoteric reaction of milk is simply explained. All milks are acid to phenolphthalein, the average degree of acidity of cow's milk being about equal to 20 c.c. of normal acid per litre; the exact degree varies slightly according to the amount of phenolphthalein used, and the temperature. The original acidity of milk is due to the free casein it contains. When lactic fermentation sets in the increase in the acidity is due, in the first place to liberation of casein from calcium caseinate and to conversion of dicalcium phosphate into the monocalcium salt; it is only after acting on these salts that the lactic acid affects methyl orange (Bordas and Touplain, Compt rend. 1911, 152, 1274; *cf.* van Slyke and Baker, J. Biol. Chem. 1919, 40, 345).

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[1] L. V. S. = Landwirthschaftliche Versuchs-Stationen.

Abnormally, milk may be bluish-white, deep-yellow, brown, pinkish-red, blue, or black in colour, watery, slimy, stringy, sandy, or heterogeneous in consistency, putrid or otherwise offensive in odour, and salty, sour, bitter, or astringent in taste.

The liquid secreted by the female immediately before or after parturition is termed colostrum or beestings, and differs considerably from normal milk in both physical and chemical characters.

Composition.—The ancients were acquainted with only three of the constituents of milk, viz. fat, casein, and water. Bartoletus of Bologna (1619) discovered a fourth constituent, the 'nitrum seri lactis,' afterwards renamed by Testi (1698) *zucchero di latte* (sugar of milk). Geoffrey (1737) separated the soluble salts and identified sodium chloride among them. Scheele (1780) found calcium phosphate in the ash.

At the present time the following substances are stated to be normal constituents of fresh milk.

(*a*) *Proteins*: Casein, opalisin (Wroblewski, Zeitsch. physiol. Chem. 1898, 308); and the mucoid-protein of Storch (Analyst, 1897, 148); albumin (lactalbumin); globulin (Sebelien, Zeitsch. Chem. 9, 445; Hewlett, J. Physiol. 1892, 13, 798; Arthus, Arch. Physiol. 1893, 673; Osborne and Wakeman, J. Biol. Chem. 1918, 33, 243).

(*b*) *Extractive matters*: Urea (Lefort, Compt. rend. 62, 190); creatinine (Weil, Ber. 11, 2175); traces of lecithin, cholesterol (0·01 to 0·018 p.c.), and hypoxanthine (Schmidt-Muhlheim, P. Arch. 30, 379)

(*c*) *Organic acids*: Lactic acid (Marchand, J. Pharm. Chim. [iv.] 29, 311; Hoppe-Seyler, Virch. Arch. 17, 443; Manetti and Musso, Zeitsch. Chem. 16, 397), though it is doubtful if this exists in perfectly fresh milk; citric acid (Henkel and Soxhlet, Bied. Zentr. 17, 787); acetic acid (Béchamp, Compt. rend. 76, 836); orotic acid (Biscaro and Belloin, Mon. Scient. [iv.] 19; i. 384; and Ann. Soc. Chim. Milano, 11, 1905).

(*d*) *Carbohydrates*: Sugar of milk, and a second carbohydrate discovered by Ritthausen (J. pr. Chem. [i.] 57, 348).

(*e*) *Other organic bodies*: Alcohol (Béchamp, Compt. rend. 76, 836); lactochrome, an organic colouring matter (Blyth, Chem. Soc. Trans. 1879, 531); and a bitter principle.

(*f*) *Inorganic acids* (*in combination*): Phosphoric, hydrochloric, sulphuric (Musso and Schmidt, Bied. Zentr. 1179, 865); thiocyanic (Musso); but its presence is accidental from mustard oil in food (Stoecklin and Crochetelle, Compt. rend. 1910, 150, 1530).

Enzymes.—A proteoclastic enzyme (Babcock and Russell, 14th Ann. Report, Wisconsin, Exp. Stat. 1897); an oxydase, a catalase (Loew, Zeit. Biol. 1902, 256; Wender, Chem. Zentr. 1903, i. 592), a reductase (Schardinger, Zeitsch. Nahr. Genussm. 1902, 1113; Reiss, Chem. Zentr. 1905, i. 604), and a kinase (Hongardy, Bull. acad. Roy. Belg. 1906, 888). Wohlgemuth and Strich (Sitzungsber. K. Akad. Wiss. Berlin, 1910, 520) state that carbohydrate and fat-splitting enzymes are present, also oxydase, reductase and catalase, but show that proteoclastic enzyme is due to bacteria; there is a glycyltryptophan enzyme. Tromsdorff (Centr. Bakt. Par. 1909, 1, 291) finds no reductase in quite fresh sterile milk. Bordas and Touplain (Compt. rend. 1909, 1057) reject the enzyme nature of peroxydase, and state that the reactions are due to casein.

(*g*) *Bases*: Potash, soda, lime, ferric oxide, magnesia, ammonia (Latschenberger, J. 14, 222).

(*h*) *Gases* (*in solution*): Carbon dioxide, oxygen, nitrogen.

The carbon dioxide content varies over a wide range: a normal value is about 10 p.c. by volume. Probably the carbon dioxide of milk is present as a mixture of 1 part of carbonic acid to 2 of sodium bicarbonate (Van Slyke and Baker, J. Biol. Chem. 1919, 40, 335). The carbon dioxide content of milk might afford a means of distinguishing heated from normal milk.

Microscopic characters.—Viewed under the microscope fresh milk appears as a clear colourless liquid in which are suspended—(*a*) milk globules and more rarely (*b*) granular bodies, the so-called colostrum corpuscles. Heidenhain (Handb. der Phys) states that the following morphological structures have been observed in human and to a less extent in cow's milk:—

(1) Semiglobular fat drops with a finely granular substance.

(2) Clear cells containing one or two fat drops and an eccentric nucleus.

(3) Round clear bodies easily coloured by eosin and picrocarmine, supposed to be free nuclei.

(*a*) The milk globules may vary in diameter from 0·01 to 0·0015 mm., but generally range from 0·005 to 0·0033 mm.

According to Bohr (J. 1880, 183) the diameter may vary from 0·0063 to 0·00014 mm.

Under the highest powers of the microscope they appear merely as more or less irregularly shaped globules of fat, without the faintest trace of a limiting membrane; nevertheless, all the earlier observers (Henle, Mitscherlich, Lehmann, Moleschott, &c.) believed in the existence of an external envelope, principally because ether, when shaken up with milk, will not dissolve out the fat unless acetic acid or potash is previously added. These substances were supposed to dissolve the enveloping membrane of the globules and release the fat. This view has been again advocated by Struve (J. pr. Chem. [ii.] 27, 249), who thinks the globules have a coat of insoluble casein; by Babcock (Milch.-Zeit. 17, 809), who states they are covered with an envelope of milk-fibrin, and by Béchamp (Compt. rend. 107, 772). Storch (Analyst, 1897, 198) affirms the existence of a semi-gelatinous membrane; but his conclusions have been adversely criticised by Richmond (Analyst, 1897, 207; 1904, 183) and Wood (American Medicine, 1907, 416).

The weight of evidence appears to be against the existence of a solid membrane. Soxhlet holds that the milk is a simple emulsion of fat particles with casein, calcium phosphate, &c., and that the addition of acetic acid or sodium carbonate deprives the casein of its emulsifying power. He found that when a small quantity of ether was added it also entered into an emulsion with the fat and casein, &c., and only separated out with extreme slowness. If a large excess of ether or a mixture of ether and alcohol is shaken up with milk, the fat is completely extracted, without any previous addition of acid or alkali, whereas benzene and chloroform, which are equally good solvents for fat, will not extract it from the globules even after the addition of potash. If acetic acid is added to the milk in quantity just sufficient to convert the phosphates present into acid phosphates, but not to coagulate the milk, the fat cannot be extracted with ether. If a current of CO_2 is then passed through the milk, coagulation ensues and the fat can very readily be extracted with ether. The CO_2 cannot be supposed to be capable of dissolving any membrane (L. V. S. 19, 118). If milk be dried in a vacuum over H_2SO_4 the fat can easily be extracted from the residue with ether, but if the residue is redissolved in water the solution resists the action of the ether.

Duclaux (Chem. Biol. 667) finds that if the globules are kept warm while under the microscope, they may be squeezed out and broken by pressing on the cover glass, and altered globules only differing in size from the original ones. Babcock (Milch.-Zeit. 15, 393) also found that if milk be heated to 100° and whipped, the globules are doubled in number but present the same microscopic outline as before. By passing milk through small orifices under great pressure (homogenising) the fat globules can be broken up into very minute particles. From the above facts it is certain that the only membrane is a liquid layer condensed round the globules by the surface tension. Refer also to De Sinety (Arch. de Phys. 1874, 479), Herer (J. 1871, 120), Hoppe-Seyler (Arch. Path. Anat. 17, 417). The milk globules consist mainly of various fats, but analysis shows the presence of traces of cholesterol, lecithin, and of a yellow colouring matter spectroscopically identical with lutein.

(*b*) The colostrum cells or corpuscles occur very sparingly in normal milk, but abundantly in the colostrum. They consist of irregular conglomerations of very small fat vesicles embedded in a granular protoplasmic matrix; occasionally one or more eccentric nuclei may be observed. They are about four or five times as large as the milk globules, the diameter varying from 0·014 to 0·055 mm. Heidenhain (Handb. der Phys.) finds that if a drop of warm perfectly fresh milk be examined on a Strecker's warm stage, and the temperature regulated to 38°C. amœboid movements of these cells can be observed resembling in all respects those of the white blood corpuscles, from which indeed Heidenhain considers them to be derived by a process of infiltration with milk fat.

The fat of these corpuscles is much more readily dissolved by ether than that of the milk globules. They are disintegrated by potash or acetic acid, iodine water colours them intensely yellow, hence they consist of very small globules of fat embedded in an albuminous substance.

Abnormal milk may contain hematin, biliary colouring matters, mucin, blood corpuscles, pus, mucus, fibrous clots, and many varieties of fungi and bacteria.

For a method of detecting abnormal milk depending on the colour produced on adding a drop of a saturated aqueous solution of dibromo-*o*-cresol-sulphon-phthalein to 3 c.c. of milk, *see* Baker and Van Slyke, J. Biol. Chem. 1919, 40, 357. On the addition of $\frac{1}{20}$ c.c. of the saturated aqueous solution of the dye to 3 c.c. of the milk a coloration is developed; greyish blue with normal milk, dark blue with a lower content of acid, and light green to yellow with a higher content. The higher content of acid may be due to formation or addition of acids, acid salts, or formaldehyde, or too great a degree of pasteurisation. If the colour is bluish, the milk is from an inflamed udder, or is watered or deprived of cream, or alkali has been added (De Vries, Analyst, 1920, 450).

Changes in milk.—Milk commences to undergo change from the moment it is drawn. If left exposed to the air it very soon loses its dissolved CO_2 and takes up oxygen. Cow's milk, in which the alkaline reaction is said to be more distinct whilst in the udder, soon shows the acid reaction markedly. On standing for a time a thick yellowish-white stratum, rich in fat, collects on the surface (cream), whilst the lower portion becomes bluish-white, poorer in fat, and increases in sp.gr. Recknagel (Bied. Zentr. 1884, 16) finds that 2 or 3 hours after the milk has been drawn the sp.gr. commences to rise, the milk attaining its maximum density in 6 hours if the temperature is kept down to 5°, but only after the lapse of 2 or 3 days at 15°. This property he considers to be due to the swelling up of the casein suspended in the milk. Vieth (Milch.-Zeit. 18, 141) found the average sp.gr. of 15 samples to be 1·0296 half an hour after milking, and 1·0309 16 hours later.

This phenomenon is chiefly, if not wholly, due to the slow solidification of the fat globules; fat in the liquid state has a density of 0·92, and when solid of 0·93, and the experiments of H. D. and S. O. Richmond (Dairy Chemistry, 338; and Analyst, 1901, 117) prove that the fat melts at about 32°–34°, and the liquid globules slowly solidify if cooled below this temperature.

If milk is cooled to 10° it acquires a viscous consistency which increases rapidly as the temperature falls. Hoppe-Seyler (Ph. C. 723) states that on standing the quantity of albumin falls and that of casein increases.

On boiling, CO_2 is expelled, and it is stated that H_2S is also given off (Schreiner, L. V. S. 22, 60; Rettger, Amer. J. Physiol. 1902, 450; Utz, Milch.-Zeit, 1903, 354). Arnold (Bied. Zentr. 1882, 131) states that unboiled milk colours tincture of guaiacum blue, but that boiled milk does not; potassium iodide and starch are rapidly turned blue by unboiled milk, but only slowly by boiled milk.

These reactions are due to the oxydase present in milk; there are, however, a large number of other reagents, which, when added to fresh milk, give on addition of a little hydrogen peroxide coloured oxidation products; among these may be mentioned paraphenylene diamine (Dupuoy, J. Pharm. Chim. 1897, 397; Storch, Bied. Zentr. 1898, 711; Leffmann, Analyst, 1898, 85); metaphenylene diamine (Richmond and Rosier, Analyst, 1900, 231); ortol (ortho methylamino phenol and quinol); Saul (Brit. Med. J. 1903, 664); benzidine (Wilkinson and Peters, Zeitsch. Nahr. Genussm. 1908, 172); most photographic developers (Macadie, Pharm. J. 1907, 207; *cf.* also Siegfeld, Zeitsch. angew. Chem. 1903, 764).

As in all fairly alkaline liquids, the alkaline reaction in cow's milk becomes more evident while hot (Soxhlet, J. pr. Chem. [ii.] 6, 1), but recovers its previous intensity on cooling. Boiled milk also coagulates less readily, and is less sensible to the action of ferments and bacilli (Richet, Compt. rend. 88, 750). Very considerable chemical change must therefore have taken place, but it is still not very clear what is the nature of this change.

According to Grosser (Biochem. Zeitsch. 1913, 48, 427) the milk from which the cream and colloids have been removed, is not appreciably affected by boiling so far as regards its freezing-point, phosphoric acid and nitrogen content, whereas in human milk the phosphorus and nitrogen sink considerably on boiling.

If heated over 60° milk acquires a slimy consistency, which has also been attributed to a change in the state of the suspended casein; this sliminess retards the subsequent separation of cream.

By heating milk to 100° (or even to lower temperatures) the rising of cream is hindered (Cazeneuve and Haddon, Bull. Soc. chim. 1895, 13, 500; Richmond and Bosely, Analyst, 1897, 95).

When milk is evaporated in a vacuum at the ordinary temperature, or at the ordinary pressure at a temperature of 50°, a skin gradually forms on the surface and is renewed as often as it is removed. This skin is due to the desiccation of the proteins by the surface evaporation, and to the concentration of the hydrogen ions. It was formerly thought to consist of albumin only (Hoppe Seyler, Virch. Arch. 17, 417), and the statement was made that, on boiling milk, the albumin separated out; but Sembritzki (Pogg. Ann. 37, 460) found that by continually removing the skin, he could obtain 1·023 p.c. of the milk in that form. Since the albumin is not present in such quantity, it follows that some other body such as casein must enter into its composition.

When milk is heated at from 130° to 150° it coagulates, the temperature varying with different samples of milk, depending on the composition of the salts of milk, caseinogen requiring a definite optimum calcium content for its maximum stability, being largely governed by the amounts of magnesium, citrates, and phosphates present (Sommer and Hart, J. Biol. Chem. 1919, 40, 137); Cazeneuve and Haddon (Compt. rend. 1895, 120, 1272) attribute this to the formation of formic acid by the action of heat on lactose; but Bardach (Monatsh. 1897, 199) shows that the formic acid produced is insufficient in quantity for this, and find that it is due to complex changes in the casein.

On slowly freezing milk, the ice first formed contains a greater proportion of fat, but the mother liquor contains more casein, milk-sugar, and salts, but if the freezing takes place quickly the fat is equally distributed (Kaiser and Schmeider, Bied. Zentr. 1887, 267).

For composition of ice formed on freezing milk, *cf.* Vieth, Analyst, 1891, 65; Bordas and de Raczkowski, Compt. rend. 1901, 133, 759; Richmond, Analyst, 1893, 53.

If, however, the milk is agitated, the milk-ice is richer than the mother liquor in slow freezing, but more watery and poorer in both solids and fat when quickly frozen (Henzold, Milch.-Zeit, 15, 461).

Souring of milk.—Under certain circumstances, the homogeneous structure of milk undergoes a change, and a curd is thrown down in the form of a flocculent or compact precipitate. This change is termed curdling or coagulation, and is caused by the development of lactic acid by the action of micro-organisms, *e.g.* the *B. acidi lactici*, which are constantly present in milk, even when drawn from the udder (Hueppe, Bied. Zentr. 85, 408), and precipitation of the casein.

Spontaneous coagulation is characterised by the gradual souring and thickening of the milk; it takes place more readily when the temperature is raised, and when the atmosphere is charged with electricity.

Soxhlet found fresh milk to coagulate in 19 hours at 39°; in 29 hours at 25°; in 48 hours at 20°; in 63 hours at 17·5°; in 88 hours at 15°; in 99 hours at 10°; and he kept milk for 14 days without much change in taste at 1°–2°.

Though the nature of the organisms varies the amount of acid produced in a given time at any temperature is fairly constant (*cf.* Thorner, Chem. Ziet. 1891, 1108; Van Slyke and Hart, Amer. Chem. J. 1904, 145). Richmond and Miller (Analyst, 1907, 144) have plotted out a curve showing the relation of acidity and time at 20°, and state that at other temperatures the form of the curve remains the same, but the time taken to reach a given point increases (or decreases) 2·075 times for each 10° above or below 20°. The curve is logarithmic up to 45° acidity, at which point a break occurs; this appears to be due to this being the point at which the micro-organisms do not increase (Revis and Payne, J. Hygiene, 1906, 216); from this point the development of acidity is expressed by another parabolic curve. Revis and Payne (*l.c.*) conclude that as milk turns sour, calcium phosphate is split off from the casein complex, and when curdling takes place practically all the calcium phosphate is removed.

Though the lactic fermentation is the most common in milk, other substances are produced by the action of micro-organisms; both *d*- and *l*-lactic acids are produced, and acetic, propionic, and butyric acids may be formed (*cf.* Kozai, Bied. Zentr. 1903, 273; Tissier and Gastling, Ann. Inst. Pasteur, 1903, 540; v. Freudenreich and Jensen, Centr. Bakt. Par. 1906, 529; Thorpe, Chem. Soc. Trans. 1905, 206; Richmond and Miller, Analyst, 1906, 317; Beyerinck, Proc. K. Akad. Wetensch. Amsterdam, 1907, 17), and succinic acid, together with ammonia and trimethylamine has been found in two cases by Kozai (*l.c.*). Alcohol in small quantities is almost always present in sour milk, and usually proteolysis occurs (*cf.* Kozai, and Richmond and Miller, *l.c.*; Pennington, J. Biol. Chem. 1908, 353).

The small quantity of citric acid present in milk is converted into acetic acid and carbon dioxide by the action of *B-lactis aerogenes*, 2 molecules of acetic acid being formed for every molecule of citric acid present. The greater number of the micro-organisms met with in milk affect the nitrogenous constituents. Most of them cause a decrease in the amount of casein; with some there is an increase in the albumin; with others a decrease in the albumin and little or no decrease in the casein (Supplee, Bull. Agric. Intell. 1918, 9, 990).

When milk is boiled for some time, *most* of the organisms contained in it are destroyed, and spontaneous coagulation cannot occur unless it is again impregnated by contact with the air. A temperature of 100° is, however, insufficient to destroy all the organisms present in milk

Duclaux (Le Lait, Paris, 1887) kept milk unchanged for 5 years by removing all the air from the vessel, and subsequently by heating to 120° for some time.

Spontaneous coagulation is retarded by the addition of antiseptics, which inhibit the action of the bacilli themselves, and also by alkaline substances which merely neutralise the acid formed by their action. As antiseptics the following substances are sometimes added to milk, viz. boric acid, salicylic acid, formaldehyde, hydrogen peroxide, benzoates, &c. (For a quantitative study of the action of preservatives, *cf.* Richmond and Miller, Analyst, 1907, 144)

When milk is pasteurised at a temperature of 62·8°C. (145°F.) for 30 minutes, it does not undergo any appreciable chemical change. The quantities of phosphoric acid, calcium, and magnesium in milk pasteurised at 68·3°C. (155°F.) are practically the same as in raw milk. The albumin is not coagulated at 62·8°C., but at 65·6°C. (150°F.) 5·75 p.c., and at 68·3°C. 12·75 p.c., and at 71·1°C. (160°F.) 30·78 p.c. of the albumin is rendered insoluble. The time required for coagulating the casein by rennin is slightly less in milk pasteurised at temperatures up to 65°C. (149°F.) than it is in the case of raw milk; at 75°C. (167°F.) the time is almost doubled. The acidity is slightly diminished in pasteurised milk (Rupp, U.S. Dept. Agric. Bureau of Animal Ind. Bull. 166, April 22, 1913, 1; J. Soc. Chem. Ind. 1913, 32, 880).

Coagulation by acids.—Most acids coagulate milk in the cold, more readily when heated. 1 p.c. of acetic acid is required to precipitate milk fully at the ordinary temperature, but 0·4 p.c. is sufficient at 35° and 0·2 p.c. at 100°. Even carbonic acid will coagulate milk at an elevated temperature. Duclaux (*Le Lait*) found that on saturating milk in the cold with CO_2 and heating it in a closed vessel at 115°–120°, coagulation ensued.

Many salts such as $NaCl$, $MgSO_4$, &c., coagulate milk. Alcohol and acetone act in a similar manner.

Coagulation by rennet.—This is by far the most important of all the methods of coagulating milk, and the phenomena merit the closest attention. Unfortunately the action is very complex, and there still exists some divergence of opinion as to its nature. The old theory, that coagulation was in this case also preceded by the formation of lactic acid, held by Simon, Liebig, Soxhlet, &c., is now entirely abandoned, and it is generally admitted that the action of rennet depends upon the specific property of a chemical ferment present in it. This was first isolated by Deschamps (Dingl. poly. J. 1840, 445), who termed it *chymosin*. Hammarsten (Bull. Soc. chim. [ii.] 22, 352) fully investigated the properties of this ferment. He found that it does not give the xanthoprotein reaction, is not precipitated by nitric acid, alcohol, iodine, tannin, nor by neutral acetate of lead, but it is precipitated by basic lead acetate. It is not coagulated at 100°, but its efficiency is destroyed. It is soluble in water and glycerol; the latter solution is precipitated by alcohol.

Hammarsten (J. Pharm. Chim. 5, 267) further proved that it could coagulate milk even in the absence of acids or of milk sugar, and that the precipitate obtained differed in many important particulars from that thrown down by acids. Heintz showed that rennet could produce coagulation even in solutions rendered alkaline with sodium carbonate, provided the temperature were raised to 65° (*cf.* Bang, Skand. Archiv. Physiol. 1911, 25, 105; abstracted in J. Soc. Chem. Ind. 1911, [i.] 826).

The ferment is inactive in the cold, and when present in only very small quantity. Hammarsten has proved that it cannot precipitate a solution of casein unless a small amount of certain soluble salts is present; the salt may be phosphate or chloride or sulphate, but it is essential to have it in solution; calcium phosphate in suspension is entirely useless. Small quantities of sodium phosphate, potassium chloride, the soluble barium, strontium, calcium, and magnesium salts promote the action of the ferment, larger quantities have, however, an adverse influence. The great majority of the sodium, potassium, and ammonium salts invariably retard the action of rennet (*cf.* Mallanby, J. Physiol. 1912, 45, 345).

Halliburton (*ibid.* 1890, 11, 448) and Ringer (*ibid.* 1891, 12, 164) have shown that the ferment splits up the protein, and the curd is precipitated owing to its insoluble lime salt.

The presence of alkalis and alkaline carbonates either delays or entirely prevents coagulation. Small quantities of acids, on the other hand (except boric), hasten the action (A. Weitzel, Arbeiten a. d. Kais. Gesundheitamt, 1902, 19, 126). 1 p.c. of lactic acid greatly accelerates coagulation (Engling, L. V. S. 31, 391).

Pawlow and Parastchouk (Verb. d. Vers. Nordicher Naturfor. u. Àrtze in Helsingfors, 1902, 28) have put forward the view that as many ferments contain a rennet-like body, rennet is not a special ferment at all, but that the property of curdling milk is shared by all proteoclastic enzymes. Sterile milk (acidity 20–22) will not clot if treated with sterile rennet in sterile vessels (Kreidl and Lenk, Biochem. Zeitsch. 1911, 36, 357).

Constitution of milk.—Chemists have hitherto been unable to agree with regard to the constitution of milk. According to some it is a solution, according to others an emulsion, and others consider it to be a mere mixture.

On filtering milk through a porous cell, the following substances occur in the filtrate in solution :—

The whole of the milk sugar, albumin and extractive matters, soda, potash, hydrochloric and citric acids (in combination), the greater part of the magnesia, about one-third the lime, and one-half the phosphoric acid present in the milk (Richmond, Analyst, 1901, 313, however, found that the albumin was removed). The bulk of the milk solids—viz. the fat, casein, lime, and phosphoric acid fails to pass through.

The question whether the fat exists in an emulsified state, or in morphologically differentiated structures has already been noticed (*v Microscopic characters*). The state of the casein, lime, and phosphoric acid, now claims attention.

Hammarsten (J. Pharm Chim. 5, 267) found that perfectly pure casein is insoluble in water, and possesses a strongly acid character It dissolves in the phosphates and carbonates of the alkalis; in the latter case CO_2 is expelled. It also dissolves in a solution of caustic soda, in lime water, and in baryta water. If the solution in lime water is neutralised with phosphoric acid and kept for some time at about 40°, it becomes milk-white in appearance, behaves on filtration like natural milk, and is coagulated by acids or rennet. Other solutions of casein were not affected by rennet, unless calcium and phosphoric acid or a few other substances were introduced.

Hammarsten also observed that milk-casein precipitated by rennet constantly contained 4–5 p.c of tricalcium phosphate, whilst that precipitated by acids contained a lesser and more variable percentage; the serum obtained from rennet also contained more proteins than that obtained from other precipitants. From these facts he concluded that casein was held in solution in milk by the neutral phosphates of the alkalis, and that the casein thus dissolved was able to take up the insoluble di- and tri-calcium phosphates and enter with them into a turgid, highly hydrated, and colloid condition which he considered the characteristic state of milk-casein, both in his artificial compound and in natural milk.

Coagulation by acids is according to this theory due to the conversion of the neutral phosphates of the alkalis into acid phosphates, which are unable to hold the casein in solution, but at the same time the acids convert part of the insoluble di- and tri-calcium phosphates, into the soluble mono-calcium salts. The milk-casein precipitated by acids is therefore poor in calcium phosphate.

The addition of lime-water to milk which normally contains a quantity of insoluble dicalcium phosphate results in the precipitation of more calcium phosphate, the insoluble phosphates under these conditions being a mixture of di- and tri-calcium phosphate; at the same time the acidity of the milk is reduced. When milk to be used for feeding infants is treated with lime-water and then diluted with water to twice its original volume, or more, the soluble calcium and phosphorus may be reduced to amounts less than those present in human milk (Bosworth and Bowditch, J. Biol. Chem. 1917, 28, 431).

Coagulation by rennet is due, according to Hammarsten, to the decomposition of the milk-casein into two proteins, one of which passes into perfect solution, whilst the other forms an insoluble compound with tricalcium phosphate (cheese). The approximate constancy of the percentage of calcium phosphate in the coagulum, and the excess of proteins in the serum, are thus accounted for (*cf.* Harris, J. Anat. and Physiol. 1894, 188).

On heating milk with an oxalate, calcium oxalate is precipitated; fluorides also easily precipitate the calcium (Arthus, Arch. Physiol. 1893, 673; Ringer and Hammarsten, *l c.*).

Milk-casein, according to Engling (L. V. S. 31, 391), is casein-tricalcium-phosphate, and is completely decomposed by acids, casein being precipitated and more or less of the calcium phosphate taken up into solution. Rennet again only partially decomposes the casein-tricalcium-phosphate. A portion of the protein is detached and goes into perfect solution as acid albuminate, and as soon as a certain quantity of this is formed its acid character determines the precipitation of the bulk of the casein and tricalcium phosphate as a *basic* salt (cheese).

Hammarsten (*l c*) has studied the properties of the soluble portion, which he calls whey-protein; it has the properties of an albumose.

Soldner (L. V. S. 35, 351) made the observation that although the reaction of milk is amphoteric, the bases in the ash of milk are very largely in excess of the acids. It seemed to him *à priori* improbable that a strongly acid body like casein should exist in milk in combination with neutral tricalcium phosphate, and that a quantity of base should be simultaneously present with no acid to neutralise it, and without imparting a basic reaction to the liquid. Hammersten (*l c.*) had found that casein was soluble in lime-water and Söldner found he could obtain two compounds of casein and lime; one containing 2·36 p.c. CaO reacts alkaline with litmus, but not with phenolphthalein, and dissolves in water to form an opalescent fluid which is not coagulated by rennet. The other compound containing 1·55 p.c. CaO, has a slight acid reaction; its solution in water forms after some time a milk-white fluid which is coagulated by rennet. Hammarsten had observed that pure casein contains 0·847 p.c. of phosphorus, and Söldner has proved that a solution of pure casein in lime-water leaves on ignition a residue of calcium pyrophosphate. Söldner therefore concludes that milk-casein is the *unsaturated compound of casein and lime* (1·55 p.c. CaO), and that it does not enter into combination with, nor has any specific solvent power for the insoluble di- and tri-calcium phosphates as such, these salts merely existing *in suspension* in the milk.

The power that *free casein* possesses of dissolving di- and tri-calcium phosphates is due to the acid nature of free casein. Just as it expels CO_2 from carbonates, &c., like other acids, so it abstracts part of the base from the insoluble phosphates, forming a soluble lime-casein compound.

According to Richmond (Analyst, 1900, 116; 1901, 313; 1902, 241) the state in which casein exists in milk has been elucidated by the study of the composition of the substance removed by filtration through a porous cell, and by the action of acids and of rennet.

There is little doubt that casein is a substituted phosphoric acid, and the amount of base in combination with the substance separated by porous earthenware is equal to one atom of sodium and one of calcium, together with half a molecule of tribasic calcium phosphate. The minimum amount of acid necessary to curdle milk on boiling is 8·3 c.c. normal hydrochloric or sulphuric acids per litre, and slightly greater amounts of weaker acids; this quantity is almost exactly equal to that required to combine with the sodium, and the precipitate contains the same amount of calcium, and calcium phosphate as the substance removed by a porous cell; the acidity of the serum is moreover equal to that of the milk. The behaviour of two acids is, however, anomalous, very much larger amounts of oxalic and phosphoric acids being required to curdle milk on boiling, the average quantities being 28·5 c.c. N-oxalic acid, and 35 c.c. N-phosphoric acid per litre; if we consider that oxalic acid removes calcium from milk as insoluble calcium oxalate, and phosphoric acid would form acid phosphates with calcium phosphate, it appears that these two acids break up the sodium-calcium casein-calcium-phosphate complex.

The action of rennet, though chiefly on the protein portion of the complex, presents many analogies to that of acids on boiling; a portion of the casein molecule is split off as 'whey protein,' and the residue is also a substituted phosphoric acid; the proportion of calcium and calcium phosphate to organic phosphorus in the precipitated curd is the same as that found in the substance separated by porous earthenware, and in the precipitate formed by the minimum quantity of acid on boiling; the sodium is, however, removed, and the difference between the acidities of the milk and the whey is almost exactly 8·3 c.c. N-acid per litre. It appears probable that the action of rennet is even more analogous to that of the minimum quantity of acid on heating, as the amount of protein precipitate in the latter case is never quite equal to that of the casein, indicating that a portion of the protein molecule is removed on boiling; further evidence that this is the case is shown by the fact that while mercury salts are very perfect precipitants of the casein of milk, they do not remove the whole of the casein from a solution that has been heated, a lævo-rotatory substance which is precipitated by phosphotungstic acid remaining dissolved.

By heating milk alone, or by centrifuging, practically no calcium or phosphoric acid is removed without a corresponding amount of organic phosphoric acid.

The action of acids in the cold is different from that on boiling; at ordinary temperatures at least 6 times the quantity required on boiling is necessary before a precipitate is obtained, and nearly the whole of the calcium and calcium phosphate is removed. At intermediate temperatures the amount of acid is less, and the removal of the inorganic constituents proportionately less.

These facts show that casein exists in milk as a complex of a sodium calcium salt combined with a molecular proportion of calcium phosphate, and that the simple derivatives consist of a similar complex, and are precipitated as acid salts, the sodium being removed. The older view that calcium phosphate was entangled or loosely combined appears to be untenable. This complex forming a solution resembling milk can be artificially prepared, and behaves towards rennet in a manner similar to milk. Casein in solution in alkalis is not curdled by rennet, but the molecule is split up, the hydrolysis proceeding much further than when rennet acts on the complex which exists in milk. This indicates that the final product of the action of rennet on the casein as it exists in milk is determined by a simple derivative which forms an insoluble acid salt.

It is not known in what state the albumin exists in the milk; it is not coagulated by raising the temperature to 70°, though it has been shown by Faber (Analyst, 1889, 144) and Stewart (Brit. Med. J. 1896, 626) that at this temperature it is converted into a form which is precipitated by acids or magnesium sulphate.

It has been stated that it is in combination with the casein, but the experiments of Richmond (Analyst, 1902, 240) appear to negative this view.

Lecithins, which are compounds of choline, glyceryl-phosphoric acid, and fatty acids such as stearic, are found in milk, and are probably of considerable importance in nutrition. They have been studied by Bordas and de Raczkowski (Compt. rend. 1902, 134, 1592; 135, 302, and 354) who state that the greatest amount is found in the first month; they show that by removing 98 p.c. of the cream 69 p.c. of the lecithin is removed, and this is confirmed by Glikin (Biochem. Zeitsch. 1909, 348). Nerking and Haensel give the quantity as 0·0109–0·0833 p.c. (Biochem. Zeitsch. 1908, 348).

Citric acid. Henkel (Bied. Zentr. 17, 787) found that on saturating the serum left after removing proteins, &c., with calcium salts, and slowly evaporating, a crystalline deposit of calcium citrate was formed. The amount of citric acid was estimated from this as 0·08–0·12 p.c.; but the quantity present is probably considerably greater.

Söldner (L. V. S. 35, 351) estimates it as 0·25 p.c., and Richmond (Analyst, 1901, 316) as 0·264 p.c.

It evidently exists as a soluble salt, since the same quantity separates out from whey and from serum (by cell filtration). The concretions in condensed milk consist of pure calcium citrate.

Salts. These consist principally of phosphates, chlorides, and citrates of the alkalis and alkaline earths. Musso also found 0·0391–0·0831 gram of sulphuric acid per litre. This would amount to 0·558–1·19 p.c. of SO_3 in the ash. Musso also found 0·0021–0·0046 gram NaCNS per litre of milk.

The amount of ash in cow's milk varies from 0·65 to 0·85 p.c.; generally from 0·7 to 0·8 p.c.

The ratio of ash : proteins : sugar is very constantly 2 : 9 : 13 in cow's milk, 1 : 5 : 10 in human, 1 : 6 : 23 in mare's milk (Vieth, Analyst, 13, 49). The following are average analyses of milk-ash :

	Percentage in milk	Percentage in ash
K_2O . . .	0·1728	24·5
Na_2O . . .	0·0868	11·0
CaO . . .	0·1608	22·5
MgO . . .	0·0243	2·6
Fe_2O_3 . . .	0·0005	0·3
P_2O_5 . . .	0·1922	26·5
Cl . . .	0·1146	15·6
SO_3 . . .	0·0061	1·0

(Fleischmann).

More sulphuric acid is actually found in the ash than that shown, but it is due to the oxidation of the sulphur in the albuminoids; only that determined by Musso is taken into account. On the other hand, a deduction must be made for increase of weight by oxidation. Fleischmann deducts 3·5 p.c. of the weight of the ash for this error.

Soldner has shown (L. V. S. 35, 351) that, owing to the excess of base present in milk-ash, the whole of the phosphorus in the casein is oxidised to phosphoric acid, and appears in the ash as calcium phosphate. From 25 to 40 p.c. of the P_2O_5 in the ash may be due to this source. The composition of the ash therefore still requires revision.

Soldner (*supra*) has made an estimate of the amounts of salts as actually existing in the milk. Assuming the presence of 0·25 p c. citric acid, he calculates :

Sodium chloride . . .	0·962
Potassium chloride . .	0·830
Monopotassium phosphate .	1·156
Dipotassium phosphate . .	0·835
Potassium citrate . . .	0·495
Dimagnesium phosphate . .	0·336
Magnesium citrate . . .	0 367
Dicalcium phosphate . .	0·671
Tricalcium phosphate . .	0·806
Calcium citrate . . .	2·133
Lime (in combination with casein)	0·465

Rona and Michaelis (Biochem. Zeitsch. 1909, 114) state that 40–50 p.c. of the calcium is diffusible, and that much of it is combined with proteins. Richmond (Analyst, 1901, 310) considers that the citrates exist in milk as dibasic salts and gives the following as the distribution of the phosphoric acid in milk :

	P.c.
P_2O_5 as casein combined with CaNa	0·0605
,, $Ca_3(PO_4)_2$ . . .	0·0625
,, R_2HPO_4 . . .	0·077
,, RH_2PO_4 . . .	0·020

Latschenberger (Monatsh. 5, 129) found 0·02106 p.c. of ammonia in milk. Sherman, Berg, Cohen, and Whitman (J. Biol. Chem. 1907, 171) give the amount as 0·004 p.c.

Schrodt and Hansen (L. V. S. 31, 55) found the amount of chlorine in the ash to be greater at the end than at the beginning of the period of lactation (17·63 p.c.). There was also relatively more soda than potash, though the total alkalis were the same.

The ash is almost always 8 p.c. of the solids not fat (Vieth, Analyst, 13, 63).

Gases in Milk.—Pflüger (Pafl. Arch. 2, 166) found :

	O	CO_2 (pumped out)	CO_2 (expelled by phosphoric acid)	N
1.	0·1	7·6	0·00	0·7
2.	0·09	7·4	0·2	0·8

v. also Hoppe-Seyler (Virch. Arch. 17, 41[illegible] Setchenow (Zeit. rat. Med. 1861, 285).

Colostrum is, immediately after parturition, a yellow or brownish-yellow dirty-looking liquid, slimy, viscous, and often heterogeneous in consistency. It has a peculiar smell, a stale salty taste, and generally a slight acid reaction. It coagulates on boiling. The sp.gr. at 15° varies from 1·040 to 1·080.

The presence of colostrum corpuscles is characteristic (*v. Microscopic characters*).

The character of colostrum rapidly changes, and the following analyses by Engling (Bied. Zentr. 1879, 214) will show this :

Time after calving	Sp gr	Total solids	Fat	Casein	Albumin	Sugar	Ash
Immediately	1·068	26·93	3·54	2·65	16·56	3·00	1·18
10 hours	1·046	21·23	4·66	4·28	9·32	1·42	1·55
24 ,,	1·043	19·37	4·75	4·50	6·25	2·85	1·02
48 ,,	1·042	14·19	4·21	3·25	2·31	3·86	0·96
72 ,,	1·035	13·36	4·08	3·33	1·03	4·10	0·82

Cf. also Vaudin (J. Pharm. Chim. 1894, 30, 337), and Sutherst (Chem. News, 1902, 1) who states that what is called albumin by Engling contains a large proportion of globulin; he finds 5·32 p.c. of this on the first day, and 2·05 p.c. on the second.

The proteins in colostrum vary greatly. Casein is always somewhat greater than in normal milk; albumin varies from a little above that of ordinary milk to over three times that amount. Globulin is always an essential constituent. Extractive N is a little higher than in ordinary milk. Engling (*l.c.* 96) states that at first colostrum contains no milk sugar, but only carbohydrates, resembling grape sugar. Sebelien and Sunde (Zeitsch. angew. Chem. 1908, 2546) find that the sugar is chiefly lactose, and suggest the presence of 0·05 p.c. of arabinose. The colostrum fat differs from ordinary butter in smell, taste, consistency, and melting-point. It melts at 40°–44°. This is due, according to Nilsson (Bied. Zentr. 17, 171) to the smaller quantity of volatile acids. Nuclein has been found up to 2 p.c. Cholesterol and lecithin also occur in some quantity. Urea is higher than in ordinary milk. Burr, Berberich, and Berg have recorded a number of analyses of colostrum. The characters of the fat were as follows: Refractometer reading at 40°, 44·3–48·8; m.p. 32°–41°; Reichert-Meissl value, 11·5–29·1; Polenske value, 1·35–3 83; saponification value, 203·1–231·4; iodine value, 21·9–44·4. The fat contained 0·8 p.c. of cholesterol and 0·025 p.c. of lecithin (Analyst, 1913, 108).

Engling found the ash of colostrum to consist of

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	Cl
7·23	5·72	34·85	2·06	0·52	41·43	0·16	11·25

The higher percentage of phosphoric acid and lime, and the low alkalis, are particularly noteworthy.

ABNORMAL MILK.

Blue milk. This is characterised by the appearance of blue spots, which gradually increase till the whole surface is covered. It is due to a bacillus (*B. cyanogenus*). If the reaction of the milk is acid the coloration is deep blue; in other cases it is a slaty blue, changing to deep blue on addition of acids. The colouring matter is identical with triphenylrosaniline (Martiny and Furstenberg, Milch.-Zeit. 10, 594).

Stringy milk. Some milk, on standing for a short time, becomes thick and stringy. It is due to a special ferment, which sets up mucic fermentation. Sound milk is infected by addition of a little of the stringy milk, but the ferment can be destroyed by heating to 65° or by the addition of strong antiseptics.

Red milk is due either to colouring matter in the food of the animal or more frequently to the presence of blood from the rupture of a small blood vessel in the udder; on warming the milk and centrifuging the blood may be separated and identified by the usual methods.

Bitter milk is principally due to the food, but it is occasionally obtained from cows just before the end of lactation.

For particulars of other abnormalities in milk, *v.* Kirchner's Milchwirthschaft. For milk in disease, *v.* Blyth's Foods, where other references will be found.

ANALYSIS OF MILK.

Specific gravity. This may be determined by the lactodensimeter, the pyknometer, or by the Westphal balance.

The lactometer or lactodensimeter. This is merely a special form of hydrometer with a large bulb and a slender stem, which is graduated from 15° to 45° corresponding to sp grs. of 1·015 to 1·045; in some forms the range is even less. The milk should be at 60°F., or if the determination is made at another temperature, the readings of the lactometer should be corrected by means of a table.

The milk should be stirred, and the instrument very gently lowered till it sinks no further. The reading of the lower edge of the meniscus should be taken.

The form of pyknometer which gives the best results with milk is the Sprengel tube—a U-tube with narrow capillary ends; this should be filled with milk, immersed in a vessel of water at 60°F. till the volume is constant, and weighed. he weight of milk divided by the weight of vater at 60°F. will give the specific gravity.

The Westphal balance consists of a counteroised thermometer of exactly 5 or 10 c.c lisplacement, suspended by a fine platinum vire from one end of a graduated lever. The hermometer or plummet is immersed in the nilk at 15° and equilibrium restored by suspending a series of riders from the lever, which is graduated for the direct reading of the sp.gr.

Determination of the total solids. About 5 grams of milk are rapidly weighed out into a tared platinum, porcelain, nickel, or aluminium dish, and dried on a water-bath till successive weighings at one hour's interval differ by less than a milligram. This generally occupies 4–5 hours.

Richmond (Analyst, 14, 121) states that the most satisfactory results are obtained by taking not more than 2 grams of milk, and drying for 1½ hours in a wide, flat-bottomed basin. Babcock (Dept. Agric. Rept. 13, pt. i. 81) dries the milk on asbestos, and very accurate results are thus obtained. For the rapid determination of total solids, Revis (Analyst, 1907, 284) adds 1 c.c. of acetone to 2·5 grams of milk in a wide basin and dries for 2 hours.

Determination of the ash. The total solid matter obtained by evaporating a portion of the milk to dryness is ignited at the lowest possible temperature until the ash is perfectly white; a barely visible red heat should be employed. If the temperature is raised to a visible red heat, serious loss may be incurred owing to the volatility of the chlorides in the ash. In a series of experiments Vieth (Analyst, 12, 60) found that the ash lost 25 p.c. in weight after heating at a bright red heat for half an hour. On heating for 5, 10, and 20 minutes respectively, the ash lost 6, 19, and 24 p.c. in weight. The percentage of chlorine in the ash was simultaneously reduced by 15½, 69, and 96 p.c. of its total amount, so that over two-thirds of the chlorides volatilise in 10 minutes, and nearly the whole in 20 minutes. The ash must not be kept even at the lower temperature longer than necessary. Vieth found that it lost 6 p.c. in weight in 30 minutes when kept at a dark-red heat.

Determination of the milk-fat. The fat is the most valuable and important constituent of milk, and its determination with exactness is therefore indispensable for commercial and analytical purposes. Formerly the dried milk solids were exhausted with ether or petroleum, the ether evaporated from the solution obtained and the fat weighed. This method is almost entirely abandoned, as 20–25 p.c. of the fat is left unextracted, and concordant results are unattainable.

The following methods are now in use:—

Gravimetric methods. In consequence of the discrepancies between the results obtained by different analysts by processes in general use in 1884–5 (Wanklyn, or modifications), the Society of Public Analysts appointed a committee to compare the principal methods then known. The report of the committee, presented in 1886, and adopted by the society, stated that 283 comparative analyses had been made, and that the most concordant, and most trustworthy results had been obtained by the use of *Adams's process.* It was accordingly resolved that public analysts should use that process in preference to any other. The advent of methods such as Schmidt's and Gottlieb's has, however, caused this recommendation to be generally ignored.

Adams's process. The original method (Analyst, 85, 48) as modified by Allen and Chattaway (*ibid.* 86, 74) is carried out as follows: A strip of blotting paper 22 inches long, 2½ inches wide, is thoroughly exhausted with ether and dried at 100°C. to constant weight. It is then rolled up into a coil of about 1 inch diameter with a piece of thin string (previously boiled with sodium carbonate) placed in a cap of (fat free) filter paper, and attached to it by means of the ends of the string. 5 c.c. of milk are distributed with a pipette over the upper surface of the coil, it is then transferred to the water oven and roughly dried on a glass plate. The dry coil is transferred to a 'Soxhlet's extractor,' and exhausted with ether, light petroleum, or carbon disulphide for 1½ to 3 hours, the fat solution evaporated to dryness and weighed.

If the milk is sour it is preferable to mix it well, transfer a portion into a tared basin, weigh, pour it on to the coil, wash out the basin with 2 or 3 drops of water, adding these also to the coil, then proceed as above.

Sour milk may also be rendered homogeneous by adding a few drops of ammonia. A definite volume may then be used (the sp.gr. being known).

There is some difficulty in completely exhausting the blotting paper before use. Richmond (Analyst, 14, 123) states that this can be very perfectly done by treating for 3 or 4 hours with alcohol containing 10 p.c. of acetic acid, in a large Soxhlet extractor.

Adams's method gives low results if the fat is in a finely divided condition, *e.g.* in homogenised milk.

Storch's method. 10 grams of milk are evaporated on pumice, which is then ground to a fine powder, and extracted in a Soxhlet extractor; the pumice is then dried and reground and further extracted. Many other substances can be used in place of pumice; thus plaster of Paris was used for many years, and if the fine grinding (the essential part of the method) is adhered to, gives excellent results, but if only broken up roughly the results are low. Nilsson recommends kaolin (Chem. Zeit. 1891, 37), but the substance which gives the best results is kieselguhr (Analyst, 14, 124).

Schmidt (Zeitsch. anal. Chem. 27, 464) takes a test tube of 50 c.c. capacity, graduated in the upper part to $\frac{1}{10}$ c.c., introduces 10 c.c. of milk, adds 10 c.c. of strong HCl, boils with shaking until the liquid turns dark brown, cools the tube in cold water, adds 30 c.c. of ether, shakes round, and, after standing, measures the volume of the ethereal solution and draws off 10 c.c. This he evaporates down in a weighed porcelain capsule on the water-bath, and finally in the air-bath at 100°C. He then weighs and calculates for the original quantity of the ethereal solution. If the process has been properly conducted, the ether separates from the aqueous solution quite clear, without the slightest turbidity. The ethereal solution as it flows out from the pipette should not show any watery drops. With proper arrangements the operations can be carried out in 15 minutes. Stokes, who has devised special forms of tube for this method (Analyst, 14, 30), finds the results by this method agree with those obtained by Adams's process.

Instead of taking an aliquot portion of the ethereal solution, as much as possible should be withdrawn, and the tube washed out with successive portions of ether; the whole of the fat is thus obtained and weighed.

Gottlieb's method (L. V. S. 40, 1). This is a modification of the method of Röse (Zeitsch. angew. Chem. 1888, 4), and is thus carried out: 10 c.c. of milk are measured into a tall, narrow cylinder, graduated in 0·5 c.c., and holding 100 c.c., 1 c.c. of ammonia (sp.gr. 0·96) is added, and then 10 c.c. of alcohol; the mixture is well shaken. 25 c.c. of ether, which need not be dry, are added, and the contents of the tube well mixed; finally 25 c.c. of light petroleum are added and the mixture again well shaken. It is essential that the contents of the tube be mixed after the addition of each reagent, or the results may be very low. The cylinder is then left for 6 hours, the volume of the ethereal solution measured, and 50 c.c. removed, evaporated, and the fat dried and weighed. Popp (Milch.-Zeitung, 1904, 20) states that 1 hour is sufficient for the separation, and that the sp.gr. of the ammonia may be varied between 0·91 and 0·96 without affecting the results.

A more rapid procedure is to follow the method as above described, as far as the addition of the light petroleum (the quantities being halved throughout if desired, though it is essential to adhere to the proportions given); the contents of the tube are mixed, allowed to stand a minute or two till separation takes place, again mixed, and allowed to separate. As much as possible of the ethereal layer is removed, and the residue of the fat extracted by three further shakings with a mixture of equal quantities of ether and light petroleum (the recovered solvent answers admirably for this purpose). The combined ethereal extracts are evaporated in a wide-necked flask, and the fat dried in the water oven, with frequent blowing in of air until the weight is constant. The fat is then washed out of the flask with a little light petroleum, and the flask with any small residue of non-fatty substance again weighed (Fahrion, Chem. Zeit. 1906, 267; Richmond, Analyst, 1908, 389). This last procedure should be applied to the fat determinations by all methods, especially the Schmidt method, if accurate results are to be obtained.

Siegfeld (Milchw. Zentr. 1906, 1) finds that 0·0029–0·0036 p.c. cholesterol and 0·0079–0·0166 p.c. lecithin are contained in the fat separated by Gottlieb's method.

The maceration method being particularly suited to the analysis of sour milk will be described later.

Volumetric methods. A number of methods have been described in which the milk is treated with a solvent which dissolves everything in the milk except the fat, and this is separated by centrifugal force into the narrow graduated neck of a bottle, and there measured. Of these it is only necessary to describe the Gerber acid method, and to mention the Sinacid and Sal alkali methods.

Gerber's acid method. The reagents employed are sulphuric acid (first proposed by Babcock, Seventh Ann. Rep. Agr. Expt. Stat. Univ. Wisconsin, 1889, 98) to dissolve the casein, and amyl alcohol the use of which was introduced by Leffmann and Beam (Analyst, 1892, 83), to assist the separation of the fat. Gerber has worked out the various details (Milch.-Zeit. 1892, 891; 1893, 363, 656; and 1895, 169), and at present the process is as follows: 10 c.c. of sulphuric acid (commercial sp.gr. 1·820–1·825; 90–91 p.c. H_2SO_4) are measured into a bottle with a long graduated stem called a butyrometer; 11 c.c. of milk are added, and 1 c.c. of amyl alcohol (sp.gr. 0·815, b.p. 128°–130°C.). It is important that this order be adhered to, as if the sulphuric acid and amyl alcohol be allowed to mix before the acid is diluted with the milk, an action resulting in the formation of amylene and other products takes place, which substances increase the apparent volume of the fat (Richmond and O'Shaughnessy, Analyst, 1899, 146; Siegfeld, Molkerei-Zeitung, 1899, 433). The butyrometer is closed by a rubber cork, and the contents well mixed by shaking, and inverting several times so that the liquid in the neck becomes thoroughly warm; the fat is brought up into the neck by centrifuging for several minutes at a speed of at least 1000 revolutions per minute. Unless the bottles have been kept warm during centrifuging, by the use of a steam turbine to drive the machine or other device, they must be placed in a water-bath at a temperature of 60°–65° for several minutes. The percentage of fat is read off directly on the scale; to facilitate reading, the bottom of the fat column can be adjusted to one of the main percentage lines, by pushing in or pulling out the rubber cork to a small extent.

Comparative tests with the Adams, Rose-Gottlieb, and Gerber (Babcock) methods for the estimation of fat in skimmed milk yielded results showing that the following modifications should be made in the last-named method: At least 25 c.c. of sulphuric acid should be used, the temperature of the testing machine should be not less than 82°, the centrifugal machine should have a disc at least 15 inches in diameter and be run at a minimum speed of 1800 revolutions per minute, and the mixture should be centrifuged for 10, 2, and 1 minute periods (McInerney and Troy, Analyst, 1921, 50).

There are many types of butyrometers, differing chiefly in the construction of the graduated stem, this being round, square, or flat, or with eccentric bore to magnify the fat layer; for the trained chemist the round stem is the best, and gives the most accurate readings, but to the untrained eye the lateral magnification of the scale appears to be more easy to read. A number of appliances for automatically measuring the sulphuric acid and amyl alcohol have been devised, which are fully described and illustrated in the various manufacturers' catalogues.

With care this method gives good results, usually agreeing within 0·1 p.c. of the figures given by gravimetric analysis. The usual faults made by untrained persons are: (i) insufficient mixing, which may lead to a clear fat layer not being obtained; (ii) insufficient centrifuging, leading to low results; and (iii) unsuitable strength of acid, which may give rise to a dark fat layer, and to errors in the result.

The layer measured is not pure fat (Richmond, Analyst, 1905, 326), partial hydrolysis takes place, and a portion of the soluble fatty acids is dissolved in the aqueous liquid; a small amount of amyl ester is formed, and also a sulpho-acid. If the conditions of the process are adhered to the volume of the fatty layer is but very slightly in excess of the true fat of the milk. As the whole of the amyl alcohol dissolves in the acid to form amyl hydrogen sulphate, a considerable margin of error in the measurement of the alcohol is without appreciable influence on the result.

The 'Sinacid' and 'Sal' methods. As strong sulphuric acid has certain disadvantages as a reagent, especially in the hands of inexperienced persons, the use of alkaline solutions to dissolve the casein has been introduced by Sichler (Milch.-Zeit. 1904, 417, Sinacid process) and Gerber (*ibid.* 1906, 4, Sal method).

The former method employs a solution containing sodium hydroxide, Rochelle salt, and sodium sulphate, whilst sodium chloride is substituted for the sulphate in the Sal method. Butyrometers, which are practically the same as those used in Gerber's acid method, are employed, and 11 c.c. of alkaline solution, 10 c.c. of milk, and 0·6 c.c. of *iso*butyl alcohol are measured into the bottles. The mixing and centrifuging are performed as in the acid method, but the temperature of the water-bath is 45°. The *iso*butyl alcohol used in this method, which is usually coloured red, blue, or green, does not dissolve in the aqueous liquid, but passes into the fat, and hence the measurement must be exact. A drawback is that the corks become slippery, and tend to come out of the bottles.

The 'Neusal' method. A solution containing sodium salicylate, a carbohydrate and *iso*butyl alcohol is employed, and 4 c.c. of this are added to 9·7 c.c. of milk, mixed, warmed to 45° and centrifuged. The results are good, but Golding (Analyst, 1911, 203) has shown that variations in the mixture give erroneous results.

Determination of milk-fat from formulæ. It has been found that the sp.gr. of milk, solids not fat, and the fat are dependent upon each other, so that if two of these quantities are known, the third can be calculated.

Numerous formula have been worked out to express the relations between the three data, many of them applicable only to particular methods of analysis, which have now been shown to be incorrect. Owing to the natural variation in composition and specific gravity of the fat and solids not fat, the method is only an approximate one.

The following formula, which, though scientifically incorrect, is simple, gives results which are near the truth:

$$\text{S.n.F.} = \frac{G}{4} + 0{\cdot}2F + 0{\cdot}14 \text{ or } T = \frac{G}{4} + 1{\cdot}2F + 0{\cdot}14$$

G=lactometer degrees, F=Fat, S.n.F.=solids not fat, T=total solids (Richmond, Analyst, 1905, 59).

Cf. Harris (Analyst, 1918, 263). Harris (Analyst, 1918, 345) gives the following formula for calculating the amount of added water in milk:

$$x = \frac{10{,}000\,N}{3N + 8{\cdot}5(100 - F)}$$

in which N=percentage of solids not fat, F=percentage of fat, (100−x)=percentage of added water (*cf.* Harris, Analyst, 1919, 43; 1919, 314).

For a table for sorting of milk samples based on a determination of sp.gr. and total solids, the fat being calculated by means of factors, depending on Richmond's formula, *see* Harris, Analyst, 1918, 375; Richmond, *ibid.* 1919, 200; Harris, 1919, 314, 317. Richmond has devised an improved slide-rule by which practically every calculation required in dairy analysis can be readily made (Analyst, 1920, 218).

Determination of the milk-sugar.—(1) *Gravimetrically, by Soxhlet's method.*—25 c.c. of milk are weighed out, diluted to 400 c.c.; 10 c.c. of a solution of copper sulphate (69·28 grams per litre) are added, then 6·5–7·5 c.c. of a solution of caustic soda standardised to precipitate an equal volume of the copper solution. The solution should still be slightly acid after the addition of the soda, and contain traces of copper. Scheibe (Milch.-Zeit. 1901, 113) recommends that 20 c.c. of a cold, saturated solution of sodium fluoride should also be added to remove lime salts. It is diluted to 500 c.c., filtered; 100 c.c. are transferred to a beaker, 50 c.c. of Barreswil's (Fehling's) solution are added, the whole boiled for 6 minutes, filtered through asbestos, washed with hot water, then twice with absolute alcohol and twice with ether. A special filter is used consisting of a calcium chloride tube, the bulb half filled with asbestos and previously dried and weighed. The tube containing the asbestos and precipitate is cleared of ether by blowing air through, and a stream of hydrogen passed through, whilst the bulb is gently heated for 5 minutes. The reduced copper is allowed to cool in a stream of hydrogen, and weighed. Soxhlet gives the following table:—

Copper obtained (milligrams)	Amount of milk-sugar (milligrams)
392·7	300
363·6	275
333·0	250
300·8	225
269·6	200
237·5	175
204·0	150
171·4	125
138·3	100

The intermediate values are obtained by interpolation.

(2) *By polarisation.*—The proteins in milk affect the determination, and must first be eliminated. This may be done by mercuric nitrate (Wiley, Amer. Chem. J. 6, 289).—Mercury is dissolved in double its weight of HNO_3 (sp.gr. = 1·42), and an equal volume of water added to the solution.

Vieth (Analyst, 1888, 63) gives the following directions: to 100 c.c. of milk 3 c.c. of this solution are added, the mixture well shaken and filtered. The clear filtrate is polarised, and the percentage of anhydrous milk sugar deduced. If a 200 mm. tube is used, the reading in angular degrees is multiplied by

$$0{\cdot}95 \times \frac{1}{1{\cdot}05} \times \frac{100 - 1{\cdot}057\mathrm{F}}{100} \times \frac{1}{\mathrm{sp.gr.}}$$

This expression reduces the readings to their value in anhydrous milk sugar; corrects for the volume of the fat (the volume of the proteins is taken as 3 c.c.), and converts percentages by volume into percentages by weight.

Richmond and Boseley (Analyst, 1897, 98) add to 100 c.c. of milk (if a 200 mm. tube is used):

3 c.c mercuric nitrate solution,

10·85 c.c. of water to reduce angular degrees to percentages of anhydrous milk sugar,

F×1·11 c.c. of water to correct for the volume of fat,

Lactometer degrees × $\frac{1}{10}$ to convert volume into weight percentages.

The reading in angular degrees gives the percentage direct.

Richmond (Analyst, 1910, 516) has shown that mercury salts do not precipitate the whole of the proteins, and recommends the addition of phosphotungstic acid to the mercuric filtrate. With whole milk the error is very small, but is important with dried milks, &c.

Patein (J. Pharm. Chim. 1904, 501) states that milk sugar cannot be estimated polarimetrically in human milk, as this contains a lævorotatory substance not precipitated by mercuric nitrate or picric acid.

The volume of the precipitate of fat and proteins may be estimated by the method of double dilution, *i.e.* making up the same quantity of milk to two different volumes, one being preferably twice the other; formulæ for correction have been worked out by Bigelow and McElroy (Amer. Chem. J. 25, 694), Wiley and Ewell (Analyst, 1896, 186), and Schiebe (Milch.-Zeit. 1901, 113). Mercuric iodide, and acetate, sodium metaphosphate, picric acid, and zinc ferrocyanide have also been proposed to precipitate the proteins (*cf.* Thibault, J. Pharm. Chim 1896, 5; Carrez, Ann. Chim. anal. 1909, 187).

The temperature during the process must be kept constant and within 15°–25° (Wiley, Analyst, 13, 196).

Stokes and Bodmer (*ibid.* 10, 12) recommend the use of Pavy's solution.

100 of milk-sugar have the same reducing power as 52 of glucose or 49·4 of cane-sugar. By this method a fair determination may be made by merely diluting the milk so that 6–12 c.c. decolourise about 40 c.c. of Pavy's solution.

Determination of the total proteins.—*Ritthausen's method* (Zeitsch. anal. Chem. 1878, 241).—The proteins are precipitated by copper sulphate and soda solution (*v. Determination of milk-sugar*). The precipitate is collected on a weighed filter, washed with a little of the clear filtrate, allowed to drain, washed with 80–100 c.c. of hot water, dried, the fat extracted, dried again at 125°–150° and weighed. The precipitate is ignited and the ash deducted. Sebelien (Zeitsch. Chem. 13, 135) points out that this method is not exact, since copper hydroxide does not give up all its water at 125°, but only on ignition. This error is avoided if at least 0·6 gram of protein is present in solution, and the ratio between the copper oxide used and the amount of protein falls between 1 3 and 1·35.

Fleischmann (Lehrbuch der Milchwirtsch. 1907, 70) states that the error introduced is 0·038 p.c. for each 1 p.c. of protein.

Almen's method. This method gives very exact results, and is particularly recommended by Sebelien (Zeitsch. physiol. Chem. 13, 135). 3–5 grams of milk are taken (2 grams of colostrum, 10 of whey), diluted with 3–4 vols. water; a few drops of solution of some salt (NaCl, $MgSO_4$, &c.), then excess of solution of tannin, is added in the cold. (The tannin solution consists of 4 grams tannin added to 8 c.c. of 25 p.c. acetic acid and 190 c.c. of 40–50 p.c. alcohol.) The precipitate is thoroughly washed with *cold* water, and the nitrogen in the filter and precipitate estimated by Kjeldahl's process. The result, after subtraction of the N in the filter, gives the protein N, and this ×6·38=total proteins (since both casein and albumin contain 15·7 p.c. N); for whey the factor 6·96 gives the most exact results.

Phosphotungstic acid may also be used to precipitate the proteins.

Total nitrogen. The total nitrogen in milk is best determined directly by Kjeldahl's method. The digestion must be somewhat prolonged to obtain the best results (Kreusler, L. V. S. 31, 248). In absolutely accurate determinations it is not advisable to calculate the total proteins from total N by multiplication by 6·37, because of the presence of nitrogenous extractive matters in the milk. Schmidt-Muhlheim found an average of 0·04–0·05 p.c. of extractive N. This is confirmed by Sebelien (*l.c.*), who finds the same average, with a minimum of 0·03 p.c. and an exceptional maximum (in colostrum) of 0·08 p.c. (N−0·04)×6·38 gives a very close approximation (Sebelien).

Separate determination of the proteins (casein, albumin, globulin, &c.). Hoppe-Seyler (Handb. der Phys. Chem. Anal.) proceeds as follows: 20 c.c. of milk are diluted with water to 400 c.c., transferred to a deep beaker, and very dilute acetic acid added until a flocculent precipitate just appears. Carbon dioxide is then passed for ¼–½ hour, and the precipitate allowed to subside for 12 hours. The solution, which should be perfectly clear, is passed through a weighed filter, the precipitate washed on with a little of the clear filtrate, allowed to drain, and washed once with distilled water. The precipitate=casein+fat. The latter is extracted as usual. The filtrate is boiled for a few minutes, when the albumin separates out; if the precipitate is not very flocculent, a few drops of very dilute acetic acid may be added. It is collected on a weighed filter, washed with cold water, and dried at 120°–125°.

The filtrate and wash-water are evaporated to the consistency of a thin syrup, the precipitate which settles out gathered on a small weighed filter, well washed with cold water, and weighed.

Van Slyke (Amer. Chem. J. 1894, 712) adds to 10 grams of milk + 90 c.c. of water at a temperature of 40°–42°, 1·5 c.c. of 10 p.c. acetic acid, and allows the liquid to stand 5 minutes; the precipitate of casein is washed, and the nitrogen estimated by Kjeldahl's method. The albumin is precipitated by boiling the filtrate, the nitrogen being estimated in the precipitate. This method has been extended by Van Slyke and Hart (Amer. Chem. J. 1903, 150). *Cf.* Hersey, J. Ind. Eng. Chem. 1916, 8, 335.

The method cannot be used for human milk nor for that of the mare and ass, because on dilution and treatment with acetic acid and CO_2 the casein separates in such a finely divided condition that it cannot be filtered. Blyth (Food: Lond. 88) uses the following modification for human milk: 100 c.c. are diluted to 400 c.c., acidified with dilute acetic acid, saturated with CO_2, and transferred to a tall beaker. A small cylindrical porous battery cell, closed by a perforated plug connected with a mercury pump, is immersed in the liquid. A good vacuum is maintained, and ultimately the whole of the solution passes through. The casein is left behind, and is washed, dried, and weighed. The albumin is precipitated by boiling, &c.

Pfeiffer and Schmidt (Zeitsch. Chem. 23, 445) modify Hoppe-Seyler's method in the following way for human milk: 20 c.c. of milk are diluted to 400 c.c., heated to 40°, acetic acid added drop by drop till a granular precipitate commences to form; CO_2 is then passed in for half an hour and the precipitate allowed to subside for 24 hours. The casein is then weighed, and the filtrate treated in the ordinary way.

Tolmatscheff's method.—(1) *Casein.* 20 c.c. of milk are saturated in the cold with crystallised $MgSO_4$ (it is best to make the crystals into a paste with water), 100 c.c. of a very concentrated solution of $MgSO_4$ are added, the precipitate filtered off, well washed with a concentrated solution of $MgSO_4$, the fat extracted, and the residue dried, weighed, and the ash deducted.

(2) *Albumin.* The filtrate and wash-water from the casein are acidified with dilute acetic acid, heated to boiling, filtered, washed, with water and alcohol, dried at 120°–125°, and weighed. Sebelien (*l.c.*) advises that in each case the N should be determined in the precipitate by Kjeldahl's process, and the albuminoid found by multiplication by 6·37. The results are accurate.

The following scheme is recommended for scientific purposes (Sebelien):—

(1) Determine total N by Kjeldahl's method.

(2) Total proteins by precipitation with tannin (N by Kjeldahl).

(3) Casein+globulin by precipitation with $MgSO_4$ (N by Kjeldahl).

(4) Casein by precipitation with dilute acetic acid (N by Kjeldahl).

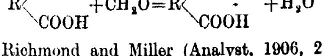
The difference between (2) and (3) gives the albumin, between (3) and (4) the globulin, between (1) and (2) the non-protein or extractive N. The latter may also be determined directly by Kjeldahl's method in the filtrate from the tannin (2).

Opalisin, which is scanty in cow's milk, but abundant in human milk, is estimated by precipitation of the casein by acetic acid, and saturation of the filtrate by sodium chloride (Wroblewski, Zeitsch. physiol. Chem. 1898, 308).

Schlossmann (*ibid.* 1896, 197) precipitates casein with a little saturated alum solution at 37°, globulin in the filtrate by saturating with magnesium sulphate, and estimates albumin from the difference between the total protein nitrogen and that of the casein and albumin.

For general review of the methods of protein estimation, *cf.* Simon, Zeitsch. physiol. Chem. 1901, 466.

Rapid estimation of proteins.—The aldehyde method. Steinegger proposed that the acidity developed in milk by the addition of formaldehyde should be used as an analytical method (Zeitsch. Nahr. Genussm. 1905, 659), and showed that it was due to the conversion of the practically neutral amino-acid groups into strongly acid methylene-amino-acid radicles.



$$R\left\langle\begin{matrix}NH_2\\COOH\end{matrix}\right. + CH_2O = R\left\langle\begin{matrix}N{=}CH_2\\COOH\end{matrix}\right. + H_2O$$

Richmond and Miller (Analyst, 1906, 224) studied the method, and pointed out that the value depended on the nature of the base used for titration, the use of soda giving lower results than strontia, which they recommend (*cf.* also Sorensen, Biochem. Zeitsch. 1907, 45).

The method is as follows: to 10 or 11 c.c. of milk (the latter volume is convenient if the Gerber fat estimation is performed) at least 1 c.c. of 0·5 p.c. phenolphthalein solution is added, and the milk neutralised with N/11 (approx.) strontia; to the faintly pink solution 2 c.c. of 40 p.c. formaldehyde solution is added, and the titration continued till a faint pink colour again appears; the acidity of the formaldehyde added is deducted, and the aldehyde figure is calculated as c.c. of N acid per litre; this multiplied by 0·170 gives the percentage of proteins in normal cow's milk. On no account must the formaldehyde solution be neutralised previous to use with soda, as the strong neutral solution becomes very appreciably alkaline on dilution; the same figure for acidity of the formaldehyde is, however, obtained when strontia is used whatever the dilution. The factor for converting aldehyde figure to proteins varies with different milks and milk products; thus it is 0·125 for whey, 0·136 for human milk, and 0·151 for asses' milk. When milk turns sour the aldehyde figure rises (Analyst, 1906, 328; and 1908, 115), due to proteolytic fermentation. The method, although extremely rapid, and approximately accurate, must be used with reservation

Acidity. By titration of milk with an alkali solution using phenolphthalein solution as indicator, a measure of the acidity is obtained; unfortunately there are several modes of expressing acidity. Soxhlet and Henkel (Chem. Zentr. 1887, 229) titrate 50 c.c of milk with N/4 soda solution, and call the number of cubic centimetres of soda used degrees of acidity; Thörner (Milch.-Zeit. 1893, 58) dilutes 10 c.c. of milk with 20 c.c. of distilled water, and titrates with N/10 soda, and expresses as degrees of acidity the number of c.c. of normal solution required per litre of milk; many others use 10 c.c of milk undiluted and titrate with N/10 solution, and express the acidity in the same terms as Thörner, but as the sodium salts of the acids present in milk dissociate on dilution the degrees determined by Thörner's method do not agree with those determined by using undiluted milk. It is not unusual, though of course incorrect, to express the acidity as grams of lactic acid per 100 c.c., and Dornic (Le Contrôle du Lait, 1897) proposes the use of N/9 soda solution (1 c.c.=0·01 gram lactic acid), and calls the grams of lactic acid per litre degrees. The amount of phenolphthalein used and the temperature have some influence on the end-point of neutrality (Richmond and Miller, Analyst, 1907, 152).

Experience has shown that the most satisfactory and concordant results are obtained by the use of strontia solution (about N/11) as the alkali at the ordinary room temperature (15°–20°), and employing at least 0·005 gram phenolphthalein for 10 c.c. of milk, and the most convenient mode of expression is c.c. of N acid per litre or degrees. The tint equal to that produced by 1 drop of an 0·01 p.c. alcoholic solution of rosaniline acetate added to 11 c.c. of milk may be taken as a standard. The normal acidity of cow's milk is about 20 degrees, and the acidity is nearly always within 2 degrees of the aldehyde figure (*q.v.*; Richmond, Analyst, 1908, 115); in a few abnormal cases it is much lower.

Analysis of sour milk. A practical method for the analysis of sour milk, by means of which the composition, when fresh, can be deduced, has been devised at the Government Laboratory. Originally described by Bell (Food and its Adulterations, 1883, pt. 2), it has been modified and placed on a scientific basis by Thorpe (Chem. Soc. Trans. 1905, 206); Richmond and Miller (Analyst, 1906, 317) have examined and criticised the method, and while suggesting a few minor modifications, agree in the main with Thorpe as to its substantial accuracy. The following is an abridged description, but for full working details the original papers should be consulted.

Maceration method for fat and solids not fat. 10 grams (*circa*) are weighed into a flat-bottomed platinum dish provided with a flattened glass stirrer, neutralised with strontia solution, using phenolphthalein as indicator, and evaporated to a stiff paste on a steam-bath; the residue is treated with successive quantities of ether, and ground up to a fine powder under the ether, which is passed through a weighed filter, and collected in a flask; the ether is evaporated and the fat dried and weighed. The fat should be washed out of the flask with light petroleum, and the residue of phenolphthalein subtracted from the weight (R. and M.). It is advisable to continue the extraction with ether and the grinding of the solids not fat till no more fat is obtained The solids not fat in the basin and on the weighed filter are dried to constant weight in the water-oven. A correction is made for the added alkali by deducting 0·00428 gram for each c.c. of N/10 strontia added.

Corrections for loss owing to decomposition.—(*a*) *The alcohol correction.* 75 grams (more or less according to the amount of sample available) are half neutralised with soda and distilled, the distillate is neutralised, using litmus paper as indicator, and redistilled, a convenient volume (say 25 or 50 c.c.) being collected, and the density taken; the difference between the density found and 1000, multiplied by 0·977, will give the quantity of anhydrous milk-sugar equivalent to the alcohol per 100 c.c. of distillate.

(*b*) *Volatile acid correction.* 10 grams of milk are half neutralised with N/10 soda, and a little phenolphthalein added; the mixture is evaporated to dryness with frequent stirring, taken up with 20 c.c. of boiling water, and titrated with N/10 soda. The difference between volume of N/10 soda used for the original acidity, and that after evaporation multiplied by 0·0255 gives the correction due to loss of milk-sugar p.c. by conversion into volatile acids.

If the milk has undergone the butyric acid fermentation, which is not common, but which is easily recognised, this method gives totally erroneous results, and the methods described by Thorpe or Richmond and Miller (*l.c.*) must be substituted.

(*c*) *Ammonia correction.* 2 grams of milk are made up to 100 c.c. with ammonia free water, and filtered clear; the ammonia is estimated by

Nesslerising in 10 c.c. of the dilute solution, the standard solution receiving an addition of 10 c.c. of a clear solution of 2 c.c. of fresh milk slightly acidified in 100 c.c. of water. The ammonia found multiplied by 500×5·2 will give the loss of casein p.c. The three corrections, of which that due to alcohol is generally by far the largest, are added to the solids not fat to obtain the solids not fat in the fresh milk.

Richmond and Miller introduce some further corrections for lactic acid, aldehyde taken up from the ether, loss of butyric acid (if present) on drying, and for hydrolysis of the proteins, but these, except in special cases, are small, and tend in opposite directions; they may be omitted, as a rule, without greatly affecting the results. Specific gravity of sour milk may be determined by adding ammonia to dissolve the curd, and making a correction for the density of the added ammonia (*cf.* Weibull, Milch.-Zeit 1894, 247, and 413; Richmond and Harrison, Analyst, 1900, 207).

ADULTERATIONS.

The principal adulterations practised are the addition of water and the removal of cream. Carbonates of the alkalis and borax, or boric acid, formaldehyde, and more rarely, salicylic acid and benzoates, are also introduced to keep milk from souring.

The addition of water or removal of cream is shown by the analysis.

Clause 4 of the Sale of Food and Drugs Act, 1899, gives power to the President of the Board of Agriculture to fix limits below which a presumption is raised till the contrary is proved that the milk is not genuine; these limits are 8·5 p.c. of solids not fat and 3·0 p.c. of fat. It sometimes happens that genuine milk yields a percentage of fat below 8·5 p.c. of solids not fat (*cf.* Wauters, Rev. internal. Falsific. 1902, 67; Malpeaux and Dorez, Ann. Agronom. 1991, 449; and Billitz, Milchw. Zentr. 1905, 113) Richmond (Analyst, 1893, 271) considered that genuine milks of this character contained above 0·7 p.c. of ash and 0·5 p.c. of nitrogen, but as he has himself found lower percentages of nitrogen (Analyst, 1903, 281, and 1910, 231) his views have undergone modification. His present view is that normal milk should contain at least 4·5 p.c. of lactose, 0·5 p.c. nitrogen, and 0·7 p.c. ash, and that abnormal milks low in solids not fat should conform to these limits in at least two of the constituents.

For the monthly variations of the composition of milk, the daily variations and the variation between morning and evening milk, *see* numerous papers in the Analyst since 1882, by Vieth and Richmond.

Soxhlet has proposed the following direct test for the addition of water, based upon the presence of nitrates in water and their total absence in milk.

The milk is coagulated by a solution of calcium chloride free from nitrate; the serum is now treated with a solution of diphenylamine in concentrated H_2SO_4, in the same way as with the ferrous sulphate test. This test has frequently been rediscovered. Szilasi (Ann. Chim. 33) measures out 1 c.c. of a solution of diphenylamine sulphate into a porcelain dish, and adds a few drops of milk; nitrates gradually give a blue coloration. These tests are not sufficiently delicate for pure water.

Fritzmann (Chem. Zentr. 1898, i. 218) adds formaldehyde and pure sulphuric acid; in the presence of nitrates a blue colour is developed.

Richmond (Analyst, 1894, 83) has found nitrates in the milk of cows that received 1 gram of potassium nitrate with their food.

Carbonates of the alkalis are best determined by taking 500 grams of milk and determining the CO_2 in the ash. The ash of pure milk should not contain more than 2 p.c.

Boric acid is detected by Meissl as follows: 100 c.c. are made alkaline with milk of lime, evaporated and incinerated. The ash is dissolved in as little concentrated HCl as possible, filtered, the filtrate evaporated to dryness, and the HCl expelled. The residue is moistened with a drop or two of an alcoholic extract of turmeric and evaporated on the water-bath. Mere traces of boric acid give a cinnabar or cherry-red coloration.

A more rapid though less delicate test consists in neutralising a quantity of milk with caustic soda, using phenolphthalein as indicator; portions of this are poured into the test tubes, and to one an equal volume of water is added, and to the other an equal volume of neutral 50 p.c. glycerol. In the presence of boric acid the glycerol tube will be much lighter in colour, usually quite white.

For a method of detecting *benzoic acid* in milk, *see* Richmond, Analyst, 1907, 32, 151; Revis, *ibid.* 1912, 37, 336, Hinks, *ibid.* 1913, 555. 25 c.c. of milk, or from 10 to 20 grams of cream are heated with an equal volume of concentrated hydrochloric acid until the precipitated curd is dissolved. The cooled mixture is shaken with 25 c.c. of mixed ether and petroleum spirit, the ethereal solution separated, 1 drop of ammonia solution and 5 c.c. of water added to it and shaken, the aqueous layer separated and tested for benzoic acid with ferric chloride (*cf.* Liverseege and Evers, J. Soc. Chem. Ind. 1913, 319).

Salicylic acid is detected by Pellett by mixing 100 c.c. of milk, 100 c.c. of water at 60°, 5 drops acetic acid, 5 drops of a solution of mercuric nitrate, filtering off the proteins, shaking with 50 c.c. of ether, allowing to settle, removing the ether, evaporating to dryness, dissolving the residue in a few drops of water, and adding ferric chloride. The quantity of salicylic acid can be approximately known by comparing the violet coloration produced with a series of standard solutions.

Boric acid is estimated (Richmond and Miller, Analyst, 1907, 144) by adding to milk half its volume of 0·5 p.c. phenolphthalein solution, and neutralising to a faint pink colour while boiling; at least 30 p.c. of glycerol is now added, and the boric acid titrated with N/10 alkali (1 c.c.=0·0062 gram H_3BO_3). R. T. Thomson (Analyst, 1893, 184) neutralises first to methyl orange, and then titrates in the presence of glycerol to phenolphthalein. Richardson and Walton (Analyst, 1913, 140) add 5 c.c. of a 5 p.c. solution of copper sulphate to 50 c.c. of the milk (or 10 grams of cream mixed with 40 c.c. of water), heat to boiling, and estimate the boric acid in the cold filtrate, by adding 2 c.c. of a 1 p.c. neutralised solution of phenolphthalein in alcohol and N/10NaOH until a certain blue shade appears, glycerol, about one-third of the volume is added and the titration with N/10NaOH continued until the blue shade again appears. 1 c.c. of N/10NaOH = 0·0071 gram boric acid. In the case of cream the fat may be estimated from the dried copper coagulum by extraction in a Soxhlet tube by light petroleum. Another method, due originally to Gooch, depends on the volatilisation of boric acid as methyl borate by distillation with methyl alcohol (*cf.* Cassal, Analyst, 1890, 230, and Hehner, *ibid.* 1891, 141). Formaldehyde may be detected by numerous methods, the most simple of which is due to Hehner (*ibid.* 1896, 94); when strong sulphuric acid is added to milk it forms a violet-blue coloration at the junction of the two liquids in the presence of formaldehyde, provided that a small quantity of an oxidising agent be present. Leonard (Analyst, 1896, 157) and Farnsteiner (Chem. Zentr. 1897, i. 133) have shown that ferric chloride is the best oxidising agent, and Rosenheim (Analyst, 1907, 106) has pointed out that this last is a tryptophan reaction.

Other tests are those of Trillat with dimethylaniline (Compt. rend. 1892, 891), Richmond and Boseley with diphenylamine (Analyst, 1895, 155), Rideal with Schiff's reagent (*ibid.* 1895, 158; *cf.* Richmond and Boseley, *l.c.*, and Hehner, *l.c.*), Mitchell with Nessler's reagent (Analyst, 1897, 97), Jorissen with morphine (Bull. Soc. chim. 1897, 17, 167), Vanino with phloroglucinol (Chem. Zentr. 1899, i. 710), Gabutti with carbazole (Boll. Chim. Farm. 1907, 349).

Preservation and Condensation of Milk.

To preserve milk for any length of time at the ordinary temperature it must be sterilised. This may be done either by means of antiseptics, such as salicylic acid, borax, or boric acid, &c. —the presence of which is highly undesirable in food—or, as is more generally practised, by the agency of heat. For the action of drugs, *v.* Soxhlet, J. Pharm. Chim. 6, 118; Mayer, Milch.-Zeit. 1882, 321. A temperature of 100° is insufficient to sterilise milk completely. Dietzell found that milk heated for 20 minutes to 105°–110° only kept sweet for a few weeks, whilst that heated to 100°–115° for 20 minutes (5 minutes at 115°) was perfectly sweet 3 years later.

Duclaux kept milk unchanged for 5 years by exhausting the air from the containing vessel and subsequently heating to 120°.

Milk can, however, be preserved unchanged by mixing it with a considerable percentage (not less than 12 p.c. of its weight) of sugar, evaporating to a semi-solid mass, and excluding the air.

The first English patent covering this process was granted to De Heine in 1810. Other English patents on condensing milk were granted to Newton in 1835, Grimway in 1847, De Lignac in 1847. A patent for a vacuum pan for evaporating milk was granted to Green in 1813 (Eng. Pat. 3754). The manufacture of condensed milk on a commercial scale was first successfully introduced in the United States of America by Borden in 1856. The Anglo-Swiss Co., which produces the larger portion of the condensed milk made in Europe and Australia, was founded in 1865–6

Fleischmann gives the following account of the process of manufacture of condensed milk *with* addition of sugar. The milk on delivery is weighed, filtered through a wire sieve, and thrown into a reservoir communicating with the tank A (Fig. 1), tapped into cans 20–30 inches deep. A number of these are placed in the water-bath B which is heated by steam from a perforated coil at the bottom, communicating with the steam-pipe F. (Beside each water-bath is a smaller bath for cleaning the cans.) When the milk has attained a temperature of 87°–94° it is transferred to the vats C or D, which have false copper bottoms, into which steam can be introduced to prevent the milk from cooling. The vat E contains the necessary quantity of cane-sugar—12 p.c. of the weight of the milk, hot milk is thrown in, stirred, and passed back to C through a filter, and this is repeated till all the sugar is dissolved.

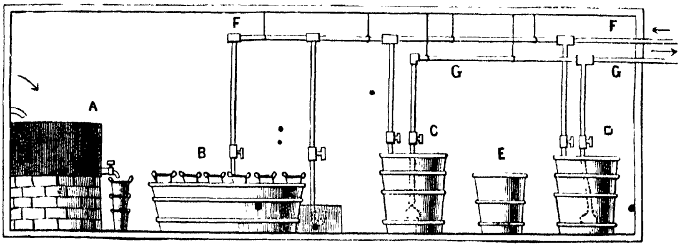


Fig. 1.

The milk in C is then sucked up by the pipe G, which terminates in a sieve, into the vacuum V (Fig. 2). This is a spherical copper vessel, with a wooden jacket round the middle and with a false bottom, into which either steam or cold water can be introduced. There is also a copper coil inside the vacuum, into which steam and cold water can be passed. A (Fig. 2) is the pipe through which the sugared milk is introduced; B is a sight-hole, hermetically closed with a thick glass plate; C is a thermometer; D a manometer; E a condenser; F the cold-water pipe for the condenser; G the pipe leading to the air-pumps; H an air-cock; I is an exhaust pipe for the condensed water; K and L are cold-water pipes for clearing the vacuum; M an exhaust pipe for the waste water from the space between the two bottoms; N an exhaust pipe for the coil inside the vacuum; O a pipe for drawing samples of milk; P the delivery pipe for the condensed milk; Q a steam pipe for supplying the space under the false bottom; R a supply pipe for the coil. On the other side of the vacuum there is another sight-hole resembling B, behind which a light is placed, whilst the progress of the operation is continually watched through B. The air-pumps are set to work, but no steam is passed in until the milk is seen to be *boiling briskly*; the temperature is then regulated to 60°. The pressure inside the vacuum is generally 60-100 mm.

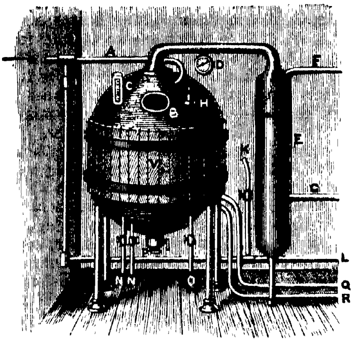


Fig 2.

When a sample taken out and cooled is of the right consistency, cold water is turned on in both the coil and false bottom, and after a short time the milk is run out and quickly cooled to 15°. It is then tapped into canisters; the covers, which are pierced with a fine hole, are soldered on—the heat of the operation causes the greater part of the residual air to be expelled, the hole is then quickly soldered over.

Various modifications of the above process are adopted. In some places, for instance, special precautions are taken to regulate the temperature of the water-bath, and the heat is not allowed to rise above 60°-75°; in others a series of ledges are arranged in the vacuum, so that the milk trickles down from one to the other and is more quickly condensed, &c., &c. Grandeau and Kramer (J Pharm. Chim. 16, 267) state that at Zurich the addition of sugar is made to the milk heated to 35°, and the temperature in the vacuum is not allowed to rise above 52°.

In many cases part of the cream is removed before condensation.

Analysis of Condensed Milk (Sweetened).

—	Nestlé	Nestle	Anglo-Swiss Co.	Anglo-Swiss Co.	Cham	Gerber & Co
Water .	15·30	24·48	24·94	25·63	27 67	23 68
Fat . .	8·85	11·33	8·90	6·13	9·33	9·74
Albuminoids	9·98	10·97	9·68	12·65	16 53	9·80
Milk-sugar .	13·62	11·19	13·29	12·50	13·20	12 93
Cane-sugar .	50·08	39 95	41·24	41·21	30·65	41 80
Ash . .	2·17	2 08	1·95	1·88	2·20	2 05

For methods of estimating sucrose in condensed milk, *see* Jolles, Analyst, 1911, 36, 28; Nowak, *ibid.* 1912, 450.

Milk Condensed without addition of Sugar.

In America the milk is filtered, heated to 60° or 70°, filtered again and condensed in a vacuum at 40°-45° to about ⅓ of its bulk. A portion of the cream is often abstracted before condensation.

This milk will not keep for more than a few days. The milk prepared at Romanshorn (Switzerland) keeps better, but the process of manufacture is not known. It is believed that the milk is heated to about 120° in its preparation, as about ⅔ of the albumin is coagulated, whilst in ordinary (sweetened) condensed milk only about half the albumin is coagulated. A portion of the cream is abstracted before condensation on account of the rancidity which a large amount of fat quickly occasions.

Scherff's process, which is in use at Stendorff, consists in first sterilising the milk by heating it to 100°-113° for 1-2 hours in sealed vessels under a pressure of 2-4 atmospheres. It is then condensed either to ½ or to ⅓ of its bulk in a partial vacuum at a temperature of 65°-70° and a pressure of 11 mm.

Voelcker gives the following analyses of unsweetened milk:

	I.	II.
Water . . .	57·96	51·72
Fat . . .	16·02	14·33
Casein . . .	8 50	11·69
Milk-sugar . .	16·32	19·51
Ash . . .	2·20	2·75

For an account of the manufacture of condensed milk, milk powders, &c., and a discussion of methods of analysis, with special reference to American and Canadian practice, *see* R. T. Mohan, Jour Soc. Chem. Ind. 1915, 34, 109.

Kephir.

Milk does not readily undergo the alcoholic fermentation by the action of yeast, though a small amount of alcohol is formed during the lactic fermentation.

In the Caucasus a special ferment (kephir grains) is used which has the property of speedily inducing alcoholic fermentation in milk. Kern (Biol. Zentr. 2, 137) found in the grains two of the organisms of ordinary yeast (*Saccharomyces cerevisiae*) and a bacillus (*Dispora caucasica*).

For the manufacture of kephir, *v.* Krannhals (J. Pharm. Chim. 14, 191), Haccius (Bied. Zentr. 1885, 265).

The milk-sugar is changed by the action of the grains partly into carbon dioxide and alcohol and partly into lactic acid; small quantities of glycerol, acetic, succinic, and butyric acids are also formed. The casein and albumin are partly peptonised.

Kephir is an agreeable nourishing drink with a slightly sour taste. It is best relished when two days old, and three days after preparation it is decidedly sour and stronger in alcohol.

König gives the following average composition of kephir:

Water	91·21
Alcohol	0·75
Fat	1·44
Sugar	2·41
Lactic acid	1·02
Casein	2·83
Albumin	0·36

Hemialbumose	0·26
Peptone	0·039
Total proteins	3·49
Ash	0·68

A simple method of making kephir consists in taking some of the good 3-days' old product, adding 4–5 parts of cow's milk, and allowing it to ferment for 2 days with occasional shaking. The consumption of kephir has made considerable progress, and it is now the custom to take it medicinally, although its preparation in reference to the production and significance of the so-called kephir grains is still obscure. In the Caucasus kephir is prepared from milk, particularly sheep's and goat's milk, in peculiar leather pipes (*burdiuks*) by adding to it kephir grains as ferment. Struve has investigated the formation of this ferment and studied its properties. Since the augmentation of the kephir grains takes place when the milk is kept in leather pipes, their growth must necessarily be affected by the milk constituents, and although it was *à priori* impossible to determine what changes the ingredients consumed during this process undergo, it was assumed that the substances belonging to the group of proteins would maintain their general type to a greater or less degree. 100 parts of the grain dried in the air gave:

Water	11·21
Fat	3·99
Peptones soluble in water	10·98
Proteins soluble in ammonia	11·32
Proteins soluble in potash	30·39
Insoluble residue	33·11

On digesting the insoluble residue in a dilute solution of potash and subjecting it to microscopical examination, it showed an intimate mixture of yeast fungi with the bacteria described by Kern under the name of *Dispora caucasica*. Struve concludes that only 33·11 p.c. of the total substance of the grains constitutes the active ferment. With kephir grains of the above composition a drink is prepared which, according to Podwisozky, contains only traces of alcohol after 24 hours' bottling, whilst in 48 hours it becomes brisk and contains a considerable amount of alcohol, the latter increasing still further after the lapse of another 24 hours. On subjecting the three drinks characterised by the difference in the duration of the fermentation to analysis it was found that although the percentage of casein was the same in each case, the latter was not completely soluble in a mixture of dilute ammonia and potash. In the solution of the casein of the kephir of one day's fermentation only traces of a precipitate were observed; the kephir 2 days old gave 0·05 p.c. and that 3 days old 0·22 p.c. of residue. Microscopical examination of the residues showed that yeast fungi only were present, bacteria or other forms of fungi being entirely absent. From this Struve infers that the fermentation of the milk is dependent upon the growth of the yeast fungus (*Saccharomyces mycoderma, Mycoderma cerevisiæ et vini*) contained in the kephir grains, whilst the bacteria *Dispora caucasica* take no active part in the fermentation. This conclusion is confirmed by the fact that the finished kephir is capable of fermenting fresh portions of milk. From the results of this investigation Struve concludes: (1) During the fermentation the yeast fungus, under the influence of the power of vegetation and of osmotic laws, enters into animal as well as vegetable tissues, and disposes them to a variety of changes. (2) The development of the yeast fungus in the interior of organic tissues may, under favourable conditions, assume the character of a special process of fermentation. (3) The effects of such a process are increased when the evolution of carbon dioxide is retarded. (4) Animal tissues into which the yeast fungus has entered exhibit in sugar solutions as well as in milk all appearances of vinous fermentation. They can therefore be used instead of kephir grains for the preparation of kephir. (5) The formation of the kephir ferment is the cause of a peculiar growth of the yeast fungus within the tissues of the leather pipes during the process of fermentation, its fungoid form being due to the development of carbon dioxide. (6) The bacteria *Dispora caucasica* must be regarded as residues of fibrils of the tissues of the leather pipes (Ber. 17, 1364; J. Soc. Chem. Ind. 3, 493).

MILK POWDER.

By evaporating condensed milk in a vacuum chamber it is reduced to a solid form. Many patents have been taken out for drying milk; Just and Hatmaker use rollers heated by steam above the temperature of 100°, the milk being fed on to them at such a rate that it is nearly dry by the time that the adhering film reaches knives touching the surface of the rollers, that remove it continuously. A small quantity of alkali is added to render the milk powder soluble in water. The rollers may be surrounded by a jacket through which a current of air passes, or from which the air is exhausted, in which case the temperature of the rollers is not so high, and a more soluble product is obtained.

Under the Stauf, Merrell-Soule, and Bevenot de Neveu patents, milk is sprayed through small orifices under pressure, into a large chamber through which warm air is passed; evaporation takes place, and the solid milk falls in very minute particles; this method produces a very soluble powder, without the addition of alkali, and the fat does not separate in oily globules, as it does from milk powders prepared by other methods. Milk powders prepared from skim milk keep well, but those containing the fat have a tendency to turn rancid or tallowy; this is partly due to oxidation, a large surface of the fat being exposed to the air, and partly to the action of the neutral enzymes of the milk, which are not destroyed at the temperatures employed.

The following are typical analyses of milk powders:

Designation	Moisture	Fat	Milk sugar	Proteins	Mineral matter
Enriched	1·4	36·8	33·8	22·8	5·2
Full cream	4·7	29·2	35·7	24·8	5·6
Half cream	4·9	16·4	43·6	28·5	6·6
Skim	3·4	2·1	54·5	31·8	8·2
Whey	2·7	0·7	76·5	14·0	8·1
Sweetened	1·6	17·7	22·6 cane sugar 38·9	15·6	3·6

Cream.

On allowing milk to stand, the fat globules rise to the surface, and form a layer on the surface; under the influence of gravity the rate of rise of the fat globules is slow, and the whole of the cream cannot be obtained before the milk turns sour. By centrifugal force the rate of motion of the fat globules can be much increased, and practically the whole of the cream removed; the modern cream separator consists of a steel bowl rotated at a high rate of speed (5000–10,000 revolutions per minute) into which the milk is fed by a central inlet tube; from this it passes to a series of chambers (usually formed by a number of conical discs—the Alfa device), in which the heavier portion—the skim milk—passes to the outside of the bowl, while the lighter fat globules collect in the centre, and escape by an outlet at the top of the bowl, the skim milk being removed from near the periphery by a series of tubes or a special chamber, and discharged at a lower level Provision is made by an adjustment of the cream outlet for varying the proportion of skim milk and cream removed, and thus the thickness of the cream.

Qualitatively cream has the same composition as milk, but differs quantitatively in containing a very much larger percentage of fat; the other constituents, except those soluble in the fat (lecithin), or those existing in the solid form (the cellular elements) are depressed in proportion to the increase of the fat.

Clotted or Devonshire cream is prepared by setting milk in pans, and when a layer of cream has risen to the surface, heating on a water-bath nearly to boiling; the cream is removed on the following day. As evaporation takes place from the surface, not only is the percentage of fat raised, but the non-fatty solids are proportionately high.

Composition of Mammalian Milk.

	Water	Fat	Sugar	Casein	Albumin	Ash
Cow	87·25	3·75	4·75	3·00	0·40	0·75
Woman	88·20	3·30	6·80	1·00	0·50	0·20
Goat	86·04	4·63	4·22	3·49	0·86	0·76
Sheep	81·31	6·86	5·23	4·62	1·00	0·98
Buffalo	82·63	7·61	4·72	3·54	0·60	0·90
Mare	89·80	1·17	6·89	1·84		0·30
Ass	90·12	1·26	6·50	1·32	0·34	0·46
Mule	91·50	1·59	4·80	1·64		0·38
Bitch	75·44	9·57	3·09	6·10	5·05	0·73
Cat	81·63	3·33	4·91	3·12	5·96	0·58
Rabbit	69·50	10·45	1·95	15·54		2·56
Llama	86·55	3·15	5·60	3·00	0·90	0·80
Camel	86·57	3·07	5·59	4·00		0·77
Elephant	67·85	19·57	8·84	3·09		0·65
Sow	82·34	6·71	4·97	5·96		1·02
Porpoise	41·11	48·50	1·33	11·19		0·57
Whale	48·67	43·67	7·11			0·46

Human Milk.

Human milk differs in important particulars from that of the cow. It is not curdled by rennet, appears thinner, and contains more sugar and less proteins.

Fat. The fat of human milk contains a very much smaller quantity of volatile acids than that of cow's milk, and a larger amount of unsaturated acids (Laves, Zeitsch. physiol. Chem. 19, 369; Ruppel, Zeit. Biol. 31, 1; Pizzi, Staz. Sper. Ag. 1894, 615; Sauvaitre, Ann. Chim. Anal. 1902, 143). The refractive index is higher, and decreases as lactation advances and free fatty acids are present (Carter and Richmond, B. M. J. 1898, 199).

Sugar. According to Radenhausen (Zeitsch. Chem. 5, 13) and Denigès (J. Pharm. Chim. [v.] 27, 413), the sugar of human milk is lactose; the last author, however, states that there is another carbohydrate which modifies the properties, whilst Denigès finds a second dextrorotatory carbohydrate present. Carter and Richmond (*l.c.*) give the specific rotatory power as 48·7°, and state that it crystallises in rhomboid plates; they consider that more than one sugar is present.

Proteins. The casein of human milk, though closely related, differs from that of cow's milk; it is not curdled by rennet, does not exist in combination with calcium phosphate, and is thrown down by acids in a very finely divided state. Dogiel (Zeitsch. Chem. 9, 591) attributes this to the small amounts of salts present; if the salts are raised to the standard of cow's milk, the casein comes down in flakes. Kobrak (Pfluger's Archiv. 1900, 69) says that it is less acid, and by repeated precipitation with acid and solution in dilute alkali, a product like the casein of cow's milk is obtained; he considers it as a nucleo-protein *plus* histon or protamine. Lehmann and Hempel (Pfluger's Archiv. 1894, 56, 558) find 1·09 p.c. of sulphur and 3·2 p.c. ash, as against 0·72 and 6·47 p.c. respectively in the casein of cow's milk. Sikes (J. Physiol 1906, 464) gives the proportion of Ca to proteins as 1·06 : 100. Wroblewski (Diss. Berne, 1894) also finds more sulphur, and states that no nuclein is present. Abderhalden and Schittenhelm (Zeitsch physiol. Chem. 1906, 458) find that whilst biological tests show that the casein of human milk differs from that of the cow, the proportion of amino-acids is very similar (*cf.* also Tangl and Czókás, Pfluger's Archiv. 1908, 534; also Abderhalden and Langstein, Zeitsch. physiol. Chem. 1910, 8, find no difference in yield of amino-acids).

Wroblewski (*ibid.* 1898, 308) states that the amount of opalisin (*q.v.*) is abundant in human milk. Camerer and Soldner (Zeitsch. Biol. 1898, 277) find 40 p.c. of unknown protein in human milk. The ratio of protein nitrogen to total nitrogen is 0·88 (Camerer and Söldner, *l.c.*), 0·91 (Munk, Virchow's Archiv. 134, 501).

Salts. Human milk contains only about 0·03 p.c. calcium and 0·029 p.c. P_2O_5 (Sikes, *l.c.*), or 0·044 p.c. P_2O_5, according to Stoklasa (Zeitsch. physiol. Chem. 1897, 343); of the P_2O_5 0·012 p.c. belongs to the proteins (Sikes). These quantities are very much lower than those found in cow's milk. Citric acid is present.

Gases. Kulz (Zeitsch. Biol. 1895, 180) finds O 1·07–1·44, CO_2 2·35–2·87, and N 3·37–3·81 p.c. by volume.

Enzymes. Oxydase does not appear to be normally present in human milk, but there is much catalase, which is destroyed at 75° (Jolles, Zeitsch. Biol. 1903, 248). A proteoclastic enzyme is also found. Béchamp (Compt. rend. 76, 836) describes an amylolytic ferment.

Composition.—The most extensive studies of the composition of human milk are those of Leeds (Chem. News, 50, 263, 280), Pfeiffer (J.

Pharm. Chim. 13, 163), Carter and Richmond (*l.c.*), Lehmann and Hempel (*l.c.*), Szilasi (Chem. Zeit. 14, 1202), Camerer and Söldner (Zeitsch. Biol. 1896, 43 and 535), and V. and J. S. Adriance (Pamphlet Abstr. J. Chem. Soc. 1899, ii. 115).

It is difficult to deduce a mean composition from the results, as human milk appears to undergo a progressive change of composition; the table below is an abstract of the results of the observers:

Date from birth	Total solids	Fat	Sugar	Proteins	Ash
1st day (colostrum)	15·7	3·0	4·0	8·3	0·4
1st week	12·9	3·5	6·1	3·0	0·3
2nd week	12·35	3·35	6·6	2·15	0·25
3rd & 4th weeks	12·1	3·4	6 75	1·75	0 22
After 1st month	11·8	3·3	6·8	1·5	0 2

The fat is the most variable of the constituents, the maximum found being 9·05 (P.) and the minimum 0·47 (C. and R.). Forster (Ber. 14, 591) states that the last portions drawn from the lowest are richer than those preceding, 1·71, 2·77, and 4·5 p.c. being found in three successive samples. Carter and Richmond, however, find, from the examination of 37 samples taken before suckling and 37 after, that there is little difference in the fat; in 15 cases the fat was higher, and in 21 cases lower, while in one (where the reaction was excessive) the composition before and after suckling was identical. The maximum difference (with a very deficient supply) was shown in a case where 0·98 p.c. was found before suckling and 4 07 p.c. after. The cases in which the fat was found higher before suckling generally occurred when the mother was lying down, and hence it would seem that the separation of cream was largely mechanical

When lactation is established the sugar usually varies between 6 and 7 p.c., though Carter and Richmond record a sample containing 8·89 p.c. and the proteins between 1 and 2 p c.

Reaction.—Human milk always appears alkaline to litmus, and the acidity to phenolphthalein averages 3 c.c. N acid per litre.

Healthy children of both sexes discharge, from their seventh to their twelfth day from birth, a white secretion from the breast (*Hexenmilch*), which resembles human milk in composition.

Milk of other Animals.

Mare's milk is white, sp.gr. 1·035 (1·034–1·036). It is much sweeter than cow's milk, but contains less fat and proteins. Mare's milk is distinguished from all others by its small amount of fat.

Koumiss is a vinous liquor made by the Tartars by the fermentation of mare's milk. It is a white, sweetish, effervescing liquid, somewhat sour when old. The sugar gradually diminishes with age, whilst the alcohol and the lactic acid increase.

It is prepared by adding 1 part of old koumiss to 10 of fresh milk, and warming for 2–3 hours to 20°–25°. Carbon dioxide then comes off, and the liquid is bottled and left to mature. (For manufacture and analyses, *v.* Vieth, Analyst, 13, 2; L. V. S. 31, 353; Biel, J. 4, 166.) A similar preparation in imitation of the true Russian koumiss is made in Switzerland and in this country from cow's milk by adding a small quantity of sugar and yeast to skim milk; it contains more sugar and less lactic acid than old Russian koumiss, and on account of the much greater proportion of casein contained in cow's milk differs considerably from that prepared from mare's milk (Phil. Trans. [iii.] 1, 861, 888).

H. Suter-Naef (Ber. 5, 286) gives the composition of Swiss koumiss (sp.gr. 1·1286), manufactured at Davos, as follows:

	In 100 grams	Per litre	
Water	90·346	1019·64	grams
Alcohol	3·210	36·23	,,
Lactic acid	0·190	2·14	,,
Sugar	2·105	23·75	,,
Albuminates	1·860	20·99	,,
Butter	1·780	20·09	,,
Inorganic salts	0·509	5·74	,,
Free carbonic acid	0·177	2·00	,,

For observations on the changes and action of Russian koumiss *v.* Jagielski (Pharm. J. [iii.] 1, 861, 885); J. T. George (Phil. Trans. [iii.] 3, 544).

Ass's milk is white, and sweeter than cow's milk. Sp gr. between 1·023–1·035.

It readily turns acid, and easily undergoes fermentation. (For composition, *v.* Table, p. 380.)

Goat's milk is white, of insipid, sweetish taste and peculiar odour. It is a little richer in solids than cow's milk. Sp.gr. 1·030–1·035. On coagulation its casein forms thick clots. (For composition, *v.* Table, p. 380.)

Sow's milk. Petersen and Oekhen (Bied. Zentr. 1897, 711; and Milch.-Zeit. 1896, 655), Henry and Woll (Ann. Rep. Ag. Exp. Stat. Wisconsin, 1897, 10), and Woll (Exp. Stat. Record, 1900, 84) have examined the milk. The average composition is

Fat	Sugar	Proteins	Ash	Solids not fat	Sp gr.
6 71	4·97	5 96	1·02	11·95	1·0389

The fat varies from 2·4 to 12·1.

Sheep's milk. Besana (Staz. Sper. Ag. Ital. 1892, 572), Hucho (Landw. Jahr. 1897, 497), Trillat and Forestieri (Compt. rend. 1902, 134, 1517; Ann. Chim. anal. 1902, 321; Bull. Soc. chim. 1903, 29, 286), Pizzi (Staz. Sper. Ag. Ital. 1894, 615; Fleischmann (Book of the Dairy, 1896, 56). Mean composition:

Fat	Sugar	Proteins	Ash	Solids not fat	Sp gr.
6·86	5·23	5·52	0·98	11·83	1·0385

Buffalo's milk. F. Strohner (Zeitsch. Nahr. Genussm. 1888, 88), W. Fleischmann (Book of the Dairy, 1896, 57), A. Pizzi (Staz. Sper. Ag. Ital. 1894, 615), Windisch (Zeitsch. Nahr. Genussm. 1904, 273), Leather (Analyst, 1901, 200, Indian Buffalo), Pappel and Richmond (J. Chem. Soc. Trans. 1891, 246, Egyptian Buffalo).

H. D. R.

MILK-SUGAR. The manufacture of milk-sugar was originally started in Switzerland, and is carried on in other countries in Europe, notably in Germany and Sweden.

In the *German system* the whey is neutralised with milk of lime and condensed about 60 p.c. in a vacuum pan to 30° or 32°B. The thick syrup is run into shallow vats and occasionally stirred during the first 10 hours. In about 2¼ hours' time the temperature should be about 20°. To separate the crystals the sticky mass is mixed with cold water and centrifuged and the lactose crystals are washed in the drum. Two-thirds of the milk-sugar is extracted in this way, the remainder being left in the syrup. The latter is heated to boiling, the coagulated albumen skimmed off, and the liquid again concentrated *in vacuô* to 35°B. After cooling, the lactose is separated and well washed, from 0·3 to 0·7 p.c. being recovered. About 4 p.c. of raw milk-sugar is obtained from the whey. To remove albumen, traces of fat, &c., the crude lactose is dissolved in water at 45° to make a syrup of 15°B., which is heated to boiling-point after the addition of 1 p.c. of powdered charcoal and 0·2 p.c. of acetic acid It is then passed while still hot through a filter-press, and the clear syrup concentrated *in vacuô* to 35°B., crystallised, and the milk-sugar separated, washed and dried in rotary inclined cylinders or in vacuum dryers. After cooling the dried milk-sugar is finely ground in a pebble mill, and packed in cases containing 100–200 lbs The percentage of refined sugar obtained from whey is 2·5–2·6 p.c.

The *Swedish system* consists in scalding fresh whey, skimming off albumen and fat, and evaporating to one-third of the original volume in an open cheese-pan. It is further concentrated *in vacuô* at 62° to a suitable consistency, and the product run into large enamelled pans with slow rotary stirrers. It cools within 48 hours to 25°. Crystallising and refining follow the German method, with the exception that some alum is added to the decolourised solution of milk-sugar before filtration (J. Pedersen, J. New Zealand Dept. of Agric. J. Soc. Chem. Ind. 1913, 247). *See also Lactose*, art. CARBOHYDRATES.

MILK-TREE WAX, COW-TREE WAX, *v.* WAXES.

MILLERITE. Nickel sulphide NiS, crystallised in the rhombohedral system. The characteristic form of the mineral is as extremely delicate hairs and needles (*i.e.* enormously elongated prismatic crystals), usually with a radiated grouping, but sometimes loosely matted together like a wad of hair. On this account it was early known as capillary pyrites. The colour is brass-yellow with a bright metallic lustre; sp.gr. 5·65. It is found in crevices in nodules of clay-iron-stone in the coal-measures near Merthyr Tydvil in South Wales and in the Saar coal-basin; with copper-ores in several mines in Westphalia and Nassau; with hæmatite in the Sterling mine at Antwerp, New York; as velvety, fibrous, encrusting masses with pyrrhotite in the Gap mine in Lancaster Co., Pennsylvania; and abundantly in quartz near Benton in Saline Co., Arkansas.

L. J. S.

MILLET. A name somewhat loosely applied to many species of grasses, growing in tropical or sub-tropical countries. As examples may be given the following:—

Great millet, *Sorghum vulgare* (Pers.). Other names given to varieties of this plant are dhurra or durra, African millet, Kaffir corn, millo maize, American broom corn and joar.

Little millet, *Panicum miliare* (Lam.).

Common millet or **Indian millet,** *Panicum miliaceum* (Linn.).

Texas millet, *Panicum texanum* (Vasey).

Sauwa millet, *Panicum frumentaceum* (Roxb.).

Japanese broom corn, *Panicum Crus-galli* (Linn.).

Golden or **Italian millet,** *Setaria italica* (Beauv.). Varieties of this constitute German millet or Hungarian grass, Japanese millet, Boer manna, and Californian green moha.

Pearl millet, *Pennisetum typhœdeum* (Rich.). Also known as Egyptian or cat's tail millet.

Polish millet, *Panicum sanguinale* (Linn.).

Koda millet, *Paspalum scrobiculatum* (Linn.).

The seeds of some varieties are used as human food, also in the preparation of certain fermented drinks, and as food for horses, cattle, and poultry. Broom corn is so called because its seed heads, after being deprived of the seeds, are employed in making brooms. The whole plants, cut green, are employed either as green fodder, or hay for farm animals.

Many of the millets grow to a height of only 2–4 feet, but Pearl millet sometimes attains 6 feet, while great millet or Kaffir corn reaches 8 or even 10 feet.

The following analyses, many of them by Church (Food Grains of India, 1886 and 1891), will serve to show the composition of the seeds of many 'millets.'

Species	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Sorghum vulgare .	12·5	9·3	2·0	72·3	2·2	1·7
„ *saccharatum*	12·8	11·8	3·0	68·3	3·0	1·1
Pennisetum typhoideum .	11·3	10·4	3·3	71·5	1·5	2·0
Setaria italica [1] .	10·2	10·8	2·9	73·4	1·5	1·2
Panicum miliare .	10·2	9·1	3·6	69·0	4·6	3·5
„ *miliaceum* [1]	12·0	12·6	3·6	69·4	1·0	1·4
„ *frumentaceum*	12·0	8·4	3·0	72·5	2·2	1·9
„ *sanguinale* .	13·4	14·9	4·1	64·5	1·1	2·0
„ *texanum* .	(?)	4·7	2·1	47·1	23·2	(?)
Paspalum scrobiculatum [1]	11·7	7·0	2·1	77·2	0·7	1·3
'Rangoon millet' .	12·4	10·6	3·1	70·3	1·4	2·2
'Millet' . .	12·9	11·1	4·5	59·5	7·5	4·5
Dhurra . .	11·5	9·0	3·8	70·1	3·6	2·0
Sorghum vulgare .	15·2	9·3	3·3	68·0	2·5	1·7
Pearl millet [2] .	9·2	12·9	5·1	68·5	2·1	2·2

The various millets are largely used as fodder plants, but cases of death among animals fed upon young plants (of *Sorghum* in particular) have been numerous. It has been shown by Dunstan and Henry (Phil. Trans. 1902, A, 399) that the young leaves and shoots of *Sorghum vulgare* contain a glucoside, *dhurrin*, which readily hydrolyses by the action of an enzyme also present in the plant, yielding *p*-hydroxybenzaldehyde, *d*-glucose, and hydrocyanic acid. Brünnich (Chem. Soc. Trans. 1903, 788) obtained as much as 2·44 grains of hydrocyanic acid from 1 lb. of green sorghum at 5 weeks old, corresponding to 13·38 grains per 1 lb. of dry matter. The amount rapidly diminishes as the plant grows: at 9 weeks old, the same sorghum only yielded 0·20 grain per 1 lb. of green material (0·76 grain HCN per 1 lb. dry matter).

Brünnich was also able to detect hydrocyanic acid in several other varieties of millet.

Willaman (J. Biol. Chem. 1917, 29, 25) states that hydrocyanic acid is present in sorghum not only as the glucoside, dhurrin, but in another form. He also finds that leaves subjected to a low temperature contain more hydrocyanic acid in both forms than ordinary leaves, thus explaining and confirming the general opinion that young sorghum is especially poisonous after a frost.

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[1] The samples were deprived of their husks before analysis.

[2] A sample grown in South Africa, highly prized as food for ostriches.

When sufficiently grown, however, the various millets afford good fodder, and the smaller varieties, nutritious and palatable hay The following are analyses of some millet hays grown in the Transvaal:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Boer manna . .	7.2	4·9	1·5	43·0	36·5	6·9
Golden millet . .	7·9	11·1	1·0	29·5	41·0	9·5
Californian green moha	8·0	10·5	1·2	35·6	35·6	9·3
Jap. broom corn .	9·6	6·8	1·2	38·8	34·8	8·8

H. I.

MILLON'S REAGENT *v.* ALBUMINOIDS.

MILORY GREEN. *Chrome green v.* PIGMENTS.

MIMETITE or **MIMETESITE.** Chloroarsenate of lead $3Pb_3As_2O_8 \cdot PbCl_2$ or

$$Pb_4(PbCl)(AsO_4)_3$$

crystallised in the hexagonal system and isomorphous with apatite and pyromorphite. It is so named, from *μιμητής*, an imitator, because of its close resemblance to pyromorphite (*q.v.*), from which it can be distinguished only by chemical tests. It is probable that some of the material that has been mined as 'brown lead-ore' has included mimetite as well as pyromorphite. The mineral often occurs as well-developed hexagonal prisms, with a yellow to brown colour, rarely quite colourless and transparent, and with a resinous lustre. Sp gr. 7·0–7·25; H. 3½. A variety called *endlichite* contains much vanadium, replacing arsenic, thus forming a passage to vanadinite. Similarly, by a replacement of arsenic by phosphorus there is a passage to pyromorphite. Curved, barrel-shaped crystals, to which the name *campylite* has been applied, were formerly found in considerable abundance at Dry Gill, near Caldbeck in Cumberland. The best crystals have been found at Johanngeorgenstadt in Saxony and Tsumeb in South-West Africa.

L. J. S.

MIMOSA *v.* PRIMULINE AND ITS DERIVATIVES.

MIMOSA BARK *v.* TANNINS.

MINASRAGRITE. A hydrated acid vanadyl sulphate $V_2O_4 \cdot 3SO_3 \cdot 16H_2O$ or

$$(V_2O_2)H_2(SO_4)_3 \cdot 15H_2O$$

crystallising in the monoclinic or triclinic system. It is readily soluble in cold water. As a blue efflorescence on patronite (*q.v.*) it is of abundant occurrence in the vanadium mine at Minasragra, near Cerro de Pasco in Peru. It is an alteration product of patronite, and actually forms on museum specimens of this mineral.

L. J. S.

MINERAL ACIDS. Acids of inorganic origin, *e.g.* sulphuric, nitric, hydrochloric, phosphoric, &c.

MINERAL ALKALI. A term originally given to soda in contradistinction to potash, which was termed the *vegetable alkali.*

MINERAL BLUE. *Antwerp blue v.* PIGMENTS.

MINERAL CAOUTCHOUC. Syn. with *Elaterite* (*q.v*).

MINERAL CARBON. *Anthracite v.* FUEL.

MINERAL CHAMELEON. *Sodium* or *potassium manganate v.* MANGANESE.

MINERAL COTTON. A name given to slag-wool.

MINERAL GREEN. *Scheele's green, Hydrocupric arsenite* $CuHAsO_3$ *v.* ARSENIC.

MINERAL INDIGO. A name given to the blue oxide of molybdenum *v.* MOLYBDENUM.

MINERAL KERMES. Amorphous antimony sulphide containing the trioxide (*v.* ANTIMONY).

MINERAL OILS *v.* PETROLEUM.

MINERAL PURPLE. *Purple of Cassius v.* GOLD, PURPLE.

MINERAL TALLOW. *Hatchettine.* A variety of fossil resin or wax resembling dysodil, ozokerite, &c.

MINERAL TURPETHUM. *Mercuric sulphate v.* MERCURY.

MINERAL WATERS *v.* AERATED WATERS; also WATER

MINERAL YELLOW. A term occasionally given to lead oxychlorides when used as pigments *v.* LEAD.

MINERVITE. A hydrated phosphate of aluminium and alkalis of somewhat variable composition but perhaps

$$2AlPO_4 \cdot (K,NH_4,H)_3PO_4 \cdot 7\tfrac{1}{2}H_2O$$

It forms snow-white, earthy or pulverulent masses, with sp.gr. about 2. Boiling water does not extract more than a trace of the alkalis, but the material is soluble in a solution of ammonium citrate. It occurs as beds, reaching a metre in thickness, in caves with bat-guano and animal remains. When first extracted it is plastic. Containing potash and ammonia in addition to phosphoric acid, it is a valuable fertiliser. The following analyses are of material from each of the localities from which the mineral has been recorded: I. Minerva grotto, Fauzan, dep. Hérault, France (A. Carnot, 1895). II. Tour-Combes grotto, Misserghin, Oran, Algeria. III. A basalt cave in the St. Paul district, island of Réunion, Indian Ocean (F. Pisani, quoted by A. Lacroix, 1910). IV. Jenolan Caves, New South Wales (J. C. H. Mingaye, 1897). V. *Palmerite* from Monte Alburno, Salerno, Italy (E. Casoria, 1904; also SiO_2 0·36, Na_2O 0·02).

	I	II	III	IV	V
P_2O_5 .	37·28	35·17	42·70	40·85	37·10
Al_2O_3 .	18·59	18·18	21·00	20·59	22·89
Fe_2O_3 .	0·83	—	2·90	0·19	1·17
CaO .	1·40	0·31	—	—	trace
MgO .	0·33	trace	—	—	trace
K_2O .	8·28	5·80	1·20	8·95	8·04
$(NH_4)_2O$	0·52	0·48	3·47	—	0·90
H_2O .	28·20	28·30	29·80	27·79	29·16
Insol. .	4·35	11·60	—	1·09	—
	99·78	99·80	101·07	99·46	99·64

L. J. S.

MINETTE. A French miner's name of local origin now applied both to an igneous rock and to an iron-ore. It was mentioned by Élie de Beaumont in 1822 (Ann. des Mines, 7, 523) and by P. L. Voltz in 1828 as being applied to a rock rich in mica met with in an iron (hæmatite) mine near Framont in the Vosges Mountains (Alsace). Possibly, however, there was here some confusion, for it seems more likely that such a term (evidently a diminutive of mine) would be used by the miners for the ore itself. Nevertheless, the name is now firmly established in petrographical literature for one of the 'mica-trap' members of the group of lamprophyres, a group of dark-coloured, fine-grained rocks occurring in igneous dykes. In this sense minette is now defined as consisting essentially of orthoclase and biotite. Such a rock contains 40–60 p.c. of silica. Besides the typical occurrences in the Vosges, it is found in Odenwald in Baden, as dykes radiating from the Shap granite in the north of England, and at many other places. It is occasionally used locally for road-metal.

The name minette is also used locally for a particular type of iron-ore extending over a wide area in Lorraine, Luxemburg, and the French department of Meurthe-et-Moselle. This is a yellowish or reddish-brown oolitic limonite forming extensive beds and lenticular masses, 10–50 metres thick, interstratified with limestones, shales, &c., of Jurassic age. The grains of limonite, measuring ¼–1 mm. across, are cemented by calcite or ferruginous clay. In some of the lower beds the ore is greenish or bluish-black, and at times strongly magnetic, though still with an oolitic structure. The grains here consist of chamosite (also known to French mineralogists as berthiérine), a hydrated silicate of aluminium and iron (FeO about 40 p.c.) belonging to the chlorite group and closely allied to thuringite (*q.v.*). This was no doubt the original mineral, which by oxidation and hydration gave rise to the limonitic ores. The ore contains Fe 30–40, CaO 5–14, SiO_2 5–20, and P_2O_5 1–2 p.c. The output in 1912 amounted to 44 million tons of ore, and the reserves approach 5000 million tons. L. J. S.

MINIUM *v.* LEAD.

MINJAK-LAGAM *v.* OLEO-RESINS.

MINJAK TENGKAWANG *v.* BORNEO TALLOW.

MIRABILITE. A mineral consisting of decahydrated sodium sulphate $Na_2SO_4,10H_2O$, crystallised in the monoclinic system, and identical with the artificially-produced Glauber's salt or *sal mirabile* of Glauber. It is deposited in abundance by the waters of certain lakes and marshes, particularly in arid regions and during the colder months of the year. In the Great Salt Lake of Utah, when in winter the temperature falls below a certain point, the water assumes an opalescent appearance due to the separation of sodium sulphate as a crystalline precipitate. Under favourable circumstances the shores of the lake become covered to a depth of several feet with crystallised mirabilite. The material is collected into heaps beyond the reach of the waves, otherwise with rising temperature the whole deposit rapidly disappears. Enormous quantities of the material are here available. Analysis gave: Na_2SO_4 42·33, H_2O 55·76, NaCl 0·63, $CaSO_4$ 0·27, $MgSO_4$ 0·02, insoluble 0·77 p.c. (G. P. Merrill, The Non-metallic Minerals, 2nd ed. New York, 1910). Extensive deposits of very pure mirabilite are also found in the dry lakes at many localities in Wyoming and California, and also in Roumania, Siberia, and Chili. Mirabilite is deposited on the floor of the Karaboghaz Gulf (Caspian Sea) during the winter months, whilst during the summer the deposit consists mainly of sodium chloride. Masses have been found on the shores of lakes in the Antarctic. The mineral also forms bedded deposits with gypsum and rock-salt in Austria, Sicily, Spain, &c. In Spain it is of wide distribution, being specially abundant in the salt deposits in the neighbourhood of Ciempozuelos, to the south of Madrid; an analysis of this material showed $Na_2SO_4,10H_2O$ 98·99 p.c. It is of rare occurrence in the Prussian salt deposits; and in England a single occurrence has been noted in gypsum beds of Permian age at Kirkby Thore in Westmorland. Since from solutions rich in sodium chloride mirabilite is formed only at temperatures below 16°C., its presence fixes a maximum point on the thermometer at which these deposits were formed. The mineral also occurs as an efflorescence in limestone caves (*e.g.* the Mammoth Cave in Kentucky); and has been formed by the action of volcanic gases on sea-water (*e.g* at Hawaii). Although mirabilite is of abundant occurrence, very little use appears to have been made of it, except locally for tanning and soap making. L. J. S.

MIRBANE, ESSENCE OF. A trade name for nitrobenzene as used in perfumery.

MISPICKEL, Arsenopyrite, or **Arsenical pyrites** (Ger. *Arsenikkies*). A mineral consisting of iron sulpharsenide FeAsS, crystallising in the orthorhombic system. The crystals are usually quite simple in form, being bounded by a longer or shorter rhombic prism and terminated by dome faces. They are isomorphous with marcasite (*q.v.*). When not tarnished, the material is tin-white in colour with a brilliant metallic lustre. Sp.gr 6·1; hardness 6. Granular and compact masses are frequent. A cobaltiferous variety (4–10 p.c. cobalt replacing iron) is known as *danaite*. The mineral is sometimes highly auriferous, and it is then a valuable ore of gold, as in New South Wales, California, and Alaska.

Mispickel occurs chiefly in mineral-veins. Large quantities are found in the silver-lead veins of Freiberg, Saxony, and in the tin veins of Cornwall and Devon. White arsenic is obtained as a by-product when these ores are roasted. L. J. S.

MITIS GREEN. *Copper aceto-arsenate, Schweinfurth green v.* ARSENIC.

MITRAGYNINE $C_{22}H_{31}O_5N$. An alkaloid found in the leaves of *Mitragyne speciosa*, a tree found in the Malay States, Borneo, the Philippine Islands, and New Guinea. An amorphous colourless solid, distilling unchanged at 230°–240°/5 mm.; m.p. 102°–106°. Forms a crystalline picrate, acetate, and trichloroacetate (Field, Chem. Soc. Trans. 1921, 887).

MITRAVERSINE $C_{22}H_{28}O_4N_2$ (?). An alkaloid found in *Mitragyne diversifolia*. Crystalline; m.p. 237°. Slightly soluble in boiling water and in sodium hydroxide solution. Forms a hydrochloride; rhomb-shaped leaflets; m.p. 208°–210°.

MITTLER'S GREEN. Syn. with *Guignet's green*, art. CHROMIUM.

MOCHA-STONE *v.* AGATE.

MOIRÉE MÉTALLIQUE. The term given to the variegated arborescent or crystalline appearance on the surface of tin plate produced by heating the plate and applying to it some dilute *aqua regia* for a few seconds, washing it with water, drying and coating it with lacquer.

MOISSANITE. Naturally occurring carbon silicide CSi, crystallised in the rhombohedral system, and identical with the artificial product known as carborundum. As minute, green, hexagonal plates, associated with microscopic diamonds, it was detected by Henri Moissan (1852–1907) in the meteoric iron of Cañon Diablo in Arizona. L. J. S.

MOLASSES *v.* SUGAR

MOLDAVITE or **BOTTLE-STONE.** A glassy substance of a clear bottle-green colour found as curiously marked and pitted pebbles in the gravels of the Moldau river in Bohemia and in other streams in Bohemia and Moravia. Sp gr 2·36; H. 5½. It contains 76–83 p.c. of silica. Analysis of a specimen from Trebitsch in Moravia gave: SiO_2 81·21, Al_2O_3 10·23, FeO 2·45, CaO 2·10, MgO 1·08, Na_2O 0·43, loss on ignition 0·04=99·54. Under the names of 'pseudo-chrysolite' and 'water chrysolite,' this material is occasionally cut as a gem-stone. Similar glasses, known as tektites, billitonites, and australites, are found in other parts of the world. There has been much discussion as to their origin; some regard them to be volcanic glass (obsidian), whilst others assert them to be of meteoric origin. The Bohemian stones have been thought to be artificial products, namely, the relics of an ancient glass making industry. (*Ref.*–F. E. Suess, Jahrb. Geol Reichsanstalt, Wien, 1900, 50; Mitt. Geol Gesell Wien, 1914, 7, 51; G. P. Merrill, Bull. U.S. Nat Mus. 1916, No. 94.) L. J. S.

MOLERA. A heat-insulating material produced in Sweden by mixing a kind of fine clay found on the island of Mors with cork-dust and firing the bricks so made.

MOLYBDENITE or **MOLYBDENUM-GLANCE.** A mineral consisting of molybdenum disulphide MoS_2, crystallising in the form of six-sided scales or short prisms, the system of crystallisation being possibly hexagonal. There is a perfect cleavage parallel to the base, and the laminæ are very flexible but not elastic. The mineral is very soft (H.=1), sectile, and greasy to the touch, and it readily marks paper. The colour is lead-grey with a bluish tinge and a metallic lustre. Sp gr. 4·7. In its scaly form and general appearance molybdenite bears a striking resemblance to graphite, differing from this, however, in the bluish tinge of its colour. It is, of course, readily distinguished from graphite by its greater density and by its chemical reactions. The name molybdenite (from μόλυβδος, lead or lead-ore) itself bears witness to the confusion between this mineral and black-lead or plumbago (graphite), and, indeed, the two minerals were not distinguished until Scheele in 1778 obtained molybdic acid from one of them. The name *jordisite* (F. Cornu, 1909) has been given to a black, powdery, colloidal form of molybdenum disulphide, found in the Himmelsfürst mine at Freiberg in Saxony, and considered to be distinct from the crystalline mineral.

As isolated scales disseminated through crystalline rocks of various kinds (granite, pegmatite, gneiss, marble, &c.), molybdenite is of wide distribution, though usually only in small amounts, and often in association with wolframite. It is also found in metalliferous veins and in quartz veins. In small quantities it has been won by mining at Altenberg in Saxony, near Flekkefjord and Egersund in Norway, Kingsgate in New South Wales, at Bamford and Wolfram Camp in the Chillagoe mining district in North Queensland, in Canada, and in the States of Washington and Arizona. It is the principal source of molybdenum, and is used for the preparation of ammonium molybdate and other compounds employed in the laboratory; for the preparation of a fine blue pigment for dyeing fabrics; and for the manufacture of ferro-molybdenum, which, combined with chrome-steel, gives a self-hardening product, especially suitable for high-speed tools. Molybdenum steel is used for rifle-barrels, guns, propeller-shafts, wire, &c.

References.—Occurrence and uses of molybdenum ores, Bull. Imp. Inst. 1908, 6, 181–191. A. W. G. Wilson, Mineral Industry, vol. 25 for 1916, New York, 1917. On molybdenite in *Queensland*: W. E. Cameron, Geol Survey, Queensland, 1904, No. 188; L. C. Ball, *ibid.* 1915, No. 248. In *New South Wales*: E. C. Andrews, Geol Survey N.S.W. Min. Resources, 1916, Publ. No. 24. In *Tasmania*: L. Hills and L. L. Waterhouse, Geol Survey, Tasmania Min. Resources, 1916, No. 1. In *Canada*: T. L. Walker, Dept. Mines, Ottawa, 1911, Publ. No. 93. In *U.S.A.*: F. W. Horton, Molybdenum, its ores and their concentration, U.S Bureau of Mines, 1916, Bull. 111; F. L. Hess, U.S. Geol. Survey, Mineral Resources. In *Norway*: E. R. Woakes, Trans. Inst. Min. Metall 1918. In the *British Isles*: Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 1916, vol. v. 2nd ed. 1917. L. J. S.

MOLYBDENUM. Sym. Mo. At.wt. 96·0 (Seubert and Pollard; Muller). This metal, the presence of which in molybdenite was first pointed out by Scheele in 1778, and which is said to have been isolated by Hjelm in 1790, is grouped under Mendeleef's classification with chromium, tungsten, and uranium, but, from the technical point of view, it may be regarded as a member of a group of heavy metals, including columbium, tantalum, tungsten, uranium, and vanadium, which occur in the oldest plutonic rocks and schists, and which are capable of imparting special properties to steel when added to it in extremely small proportions.

Molybdenum owes its name to the word *molybdæna*, under which title most minerals resembling lead in appearance were formerly known, and its nature and value were for long so little recognised that its principal source, the sulphide (MoS_2) was frequently passed over by the prospector as being merely graphite, which it closely resembles.

Molybdenum occurs in *molybdenite* MoS_2, *wulfenite* $PbMoO_4$, and *molybdite* (*molybdic ochre*) $Fe_2(MoO_4)_3 7\frac{1}{2}H_2O$, and in the extremely rare minerals *powellite* MoO_4, *belonesite* $MgMoO_4$, and *pateraite* $FeCo(Mo)O_4$. It also occurs in small quantities in other minerals containing the rare heavy metals of the same group, but is probably more an accidental occurrence than an essential constituent. *Ilsemanite*, another extremely rare mineral, has been described by H. F. Vance (Chem. and Met. Eng. 1918, 19, 186) as a blue compound, soluble in water, having the composition $MoO_2 4MoO_3, 6H_2O$ (*see also* J. Soc. Chem. Ind. October, 1918).

Practically the whole of the world's production of molybdenum metal and its compounds is obtained from molybdenite, although a notable amount of wulfenite is mined annually (chiefly in the United States) and treated commercially. Molybdenite is found in many localities, but the chief sources are, in order of importance, Australia (Queensland and New South Wales), Norway, Canada, Japan, and the United States. Its occurrence has also been reported in Bolivia, South Africa, New Zealand, &c. The world's production is probably under 300 tons of concentrates per annum, but is increasing. The Mineral Industry, 1918, contains a useful summary on the occurrence of molybdenite, and E. R. Woakes deals fully with Norway in Trans. Inst. Min. and Met. 1918.

Until within the last few years, molybdenite was chiefly produced by hand-picking from pegmatite and other granite rocks, and from schists in which it occurs as sparseley distributed flakes resembling high-grade graphite in appearance and general physical properties. It was formerly only purchased when of high quality (90–95 p.c. MoS_2, equivalent to 54–57 p.c. Mo), and commonly by inspection and not on assay. At the present time, the demand, although somewhat irregular, is increasing, and it is purchased on the usual commercial basis of so much per unit (*i.e.* per cent. per ton) of MoS_2 with a guarantee of not more than very small amounts of arsenic, bismuth, phosphorus, antimony, or copper. The limit fixed for these objectionable impurities is always subject to special agreement, and largely depends upon the supply available at the time of purchase. The usual grade of concentrate is 75–85 p.c. MoS_2, for which the Ministry of Munitions during the war fixed the price at 105s. per unit in England, which is very near the price ruling before the war. This price was fixed by arrangement between the Imperial and Colonial Governments, an exception being made in the case of Canada, where advantage was allowed to be taken of the higher price ruling in the United States. Particularly in Norway, where the prices have been abnormally artificial since the war, very low-grade deposits have been worked containing as little as 0·3 p.c. MoS_2. The irregularity of supply no doubt restricts the use of molybdenum in the steel industry, and, on the other hand, the uncertainty of demand does not encourage the systematic working on a big scale of the low-grade deposits which occur in enormous quantities in Canada, Australia, the United States, and elsewhere.

The majority of the larger deposits of molybdenite now worked are low in grade, ranging from ½ to 2½ p.c. MoS_2. Concentration by shaking tables is not applicable to the ores, as the flakes of molybdenite float to a large extent on the surface of the water and are lost in the tailing. When the flakes or crystals occur in sufficient size, a high-grade concentrate can be made by merely crushing the ore coarsely on rolls and screening the flakes on a sieve; the losses are heavy, however, owing to the more finely divided mineral passing with the gangue through the sieve. Practically the only method of concentration applicable on the commercial scale is that of oil (and possibly water) flotation, by which means a very high recovery of the MoS_2 is commonly obtained. When associated with other sulphides, such as copper, bismuth, ordinary iron, and arsenical pyrites, a selective flotation of molybdenite can be successfully effected within limits, but in the case of some ores, *e.g.* the molybdenum-bismuth ores of Queensland, even in the best practice the molybdenite concentrate may contain up to 5 p.c. bismuth. Direct roasting—volatilisation has recently been suggested as a means for the concentration of low-grade molybdenite ores, the volatile MoO_3 being sublimed and condensed in flues.

Metallic molybdenum may be prepared by reduction of molybdic acid MoO_3, or, preferably, of the less volatile oxide MoO_2, with carbon or by the alumino-thermic process, or by heating the oxides or chlorides in a current of hydrogen, or by the direct reduction of the sulphide by carbon in the electric furnace. The usual method for producing pure molybdenum is to roast the molybdenite to oxide, dissolve in ammonia, filter, drive off the ammonia, and reduce the resulting oxide by means of hydrogen in an electric resistance furnace. The production of ductile molybdenum is carried out in a similar manner to that of tungsten. For the manufacture of special steels, molybdenite is almost invariably used in the form of the ferro-alloy. Ferro-molybdenum is produced by the direct reduction of molybdenite, in the electric furnace, in admixture with carbon and lime:

$$2MoS_2+2CaO+3C=2Mo+2CaS+2CO+CS_2$$

Sometimes iron oxide is also added. Reduction by means of silicon metal or ferro-silicon is said to have been adopted in one American works:

$$MoS_2+Si=Mo+SiS_2$$

Lime is sometimes added to help to slag the sulphur as calcium sulphide (R. M. Keeney, Bull. Amer. Inst. Min. Eng. August, 1918). The usual commercial ferro-molybdenum contains from 80 to 85 p.c. Mo, 10 to 15 p.c. iron, 2 to 4 p.c. carbon, and 0·1 to 0·5 p.c. sulphur. The readiness with which carbides are formed probably accounts for the high proportion of carbon first present in the metal and alloy, necessitating the decarburisation with molybdenum oxide or (in the case of the ferro-alloy) with a lime slag and oxide of iron. When wulfenite is the source of supply, the mineral, which usually contains from 16 to 20 p.c. MoO_3, is fused with sodium carbonate and carbon for the production of a lead bullion and a sodium molybdate slag. Ferro-molybdenum is made by smelting the slag in an electric furnace with iron oxide and using lime as a flux (R. M. Keeney, *l.c.*).

Molybdenum, produced in the electric furnace, is brittle, and hard enough to scratch glass, properties due probably to the presence of carbon in the form of a carbide. As obtained by the reduction of the oxide by hydrogen, it is a grey powder which, on heating, sintering, and swaging at a high temperature, becomes a silver-white metal having a sp.gr. of about 10. Its m.p. is 2450°±30° (Pirani and Meyer), 2410° (Guertler and Pirani), *i.e.* between platinum and tungsten. The worked metal is malleable and ductile, and is sufficiently soft to be filed and polished. Similarly to tungsten, it may be drawn into fine wire which has approximately half the tensile strength of the corresponding size of tungsten wire. Drawn molybdenum wire has a resistivity of 5·6 microhms per c.c. at 25°C. (temp. coeff. 0·005). Annealed wire has the value of 4·8 microhms. The specific heat of molybdenum is 0·072 at 93°C., 0·074 at 280°C., and 0·072 at 440°C. (Defacqz and Guichard, Ann. Chim. 1901, 24, 139). Molybdenum is unaffected by air or water at ordinary temperatures, but is slowly oxidised by steam or when heated in presence of air. It is attacked by the halogens and by most acids and fused salts, especially oxidising salts, such as nitrates and chlorates. Hydrochloric acid has but little action, and sulphuric acid attacks it only when hot and concentrated. Carbides are formed by the action of methane or carbon monoxide on the metal at a red heat.

The chief use of molybdenum is, in conjunction with chromium, manganese, and other metals, in the manufacture of special steel, such as armour plate and projectiles, gun and rifle linings, permanent magnets, propeller shafts, &c. It is not now used to any extent in high-speed tool steels, but is said to form a constituent of the new cobalt-chromium cutting material. For the influence of molybdenum on iron, *see* L. Guillet, Rev. Mét. July, 1904; J. O. Arnold and A. A. Read, Inst. Mech. Eng. November, 1915; and Sir R. A. Hadfield, *ibid.*, A. H. Hunter, Am. Iron and Steel Inst., May 1, 1921.

The effect of molybdenum in steel is usually stated to be similar to that of tungsten, except that it is from two to four times as powerful. It is a question, however, if sufficient research has been carried out to enable it to be said that the one metal is replaceable by the other. Very little work has been done to determine the effect of molybdenum, when alloyed with non-ferrous metals. The pure metal is used in the form of wire as a filament support in incandescent electric lamps, and in electrical contact making and breaking devices in X-ray tubes, and for a winding for electrical resistance furnaces. Its use has also been suggested as a substitute for platinum and palladium in jewellery. Salts of molybdenum are used for a number of purposes, one of the most important being ammonium molybdate used as a laboratory reagent and, it is said, as a preservative for cordite.

W. G. W.

COMPOUNDS OF MOLYBDENUM.

Oxides. Molybdenum forms a series of oxides, which, during their formation in solution, often show changes of colour through various shades of blue to black or violet-black. The following are the best known oxides:—

The sesquioxide Mo_2O_3, formed when one of the higher oxides is treated with sodium amalgam or zinc, is a black powder, which forms black or dark grey salts. These salts give black or dark purple solutions when concentrated, but on dilution, the solutions become transparent and of a purple tint. They have a styptic taste, oxidise somewhat in the air, and are precipitated by alkalis forming the brownish-black hydroxide $Mo(OH)_3$ (Muthmann and Nagel, Ber. 1898, 31, 2009).

Molybdenum dioxide MoO_2 is formed by heating the sesquioxide in air or by heating the trioxide in a current of hydrogen at 470° and in other ways (Guichard, Compt. rend. 1899, 129, 722; *ibid.* 1900, 131, 998; Friedheim and Hoffmann, Ber. 1902, 35, 791; Chapman and Law, Analyst, 1907, 32, 250). It is a brown or violet-brown crystalline powder, which, like the other oxides, is reduced to metallic molybdenum when heated at 600° in hydrogen. It gives unstable salts, the concentrated solutions of which are black, but turn, successively, bluish-green, greenish-yellow, red and yellow on dilution. The hydroxide $Mo(OH)_4$ is dark red and forms a yellow or red colloidal solution in water.

Molybdenum trioxide MoO_3 is usually found with molybdenite and occurs as molybdic ochre, either as an earthy powder or incrustation, or in crystalline masses of sp.gr. 4·696 at 26°/4°. It is obtained by roasting the powdered mineral with quartz sand, treating the mass with ammonia, and after removing impurities, converting the ammonium molybdate thus formed into the trioxide by decomposition and evaporation with nitric acid (Wöhler, Annalen, 1856, 100, 376; Muthmann, *ibid.* 1887, 238, 117; Eng. Pat. 5821, 1909). It is a white powder, which becomes yellow on heating, melts at 791° to a yellow liquid, and readily volatilises in the air (Groschuff, Zeitsch. anorg. Chem. 1908, 58, 113). Towards strong acids the trioxide acts as a base (Guichard, Compt. rend. 1906, 143, 744), but generally it behaves as an acid forming oxide.

Molybdic acid $H_4Mo_2O_5$ or $MoO_3{\cdot}2H_2O$ (Mylius, Ber. 1903, 36, 638; Rosenheim and Bertheim, Zeitsch. anorg. Chem. 1906, 50, 320; Graham, Journ. Franklin, Inst. 1907 163, 69) is obtained as yellow crusts, and forms colloidal, or, according to Wohler and Engels (Zeitsch. Elektrochem. 1901, 16, 693) semi-colloidal solutions (Graham, Chem. Soc. Trans. 1864, 326; Sabanéeff, J. Russ. Phys. Chem. Soc. 21, 515). When reduced by metallic molybdenum, in neutral or faintly acid solution, the blue oxide or molybdenum molybdate is formed, but if the solution is strongly acid a brown oxide appears (Guichard, *l.c.*).

The normal molybdates are unstable and readily form polymolybdates by uniting with further molecules of the trioxide and also with other acidic oxides to form a large number of complex molybdates (Wempe, Zeitsch. anorg. Chem. 1912, 78, 298). For the constitution of the para-molybdates, *see* Copaux Compt. rend. 1913, 156, 1771. A large number of alkaline and other molybdates are known, some of which are used for the production of pigments and dyes, in pottery glazes and in analytical work. For complex molybdates of the rare earths, *see* Barbieri Accad. Lincei, 1911, [v.] 20, i. 18, *ibid.* 1916, [v.] 25, i. 775.

Molybdenum molybdate (molybdenum blue or molybdenum indigo) is obtained by reducing molybdic acid as above or with other reducing agents or by adding a cold dilute hydrochloric acid solution of molybdenum dioxide to a similar solution of ammonium molybdate and washing with sodium chloride (Guichard, Compt. rend. 1900, 131, 389, 419). Its solubility, and possibly its composition, depend on the mode of formation (Klason, Ber. 1901, 34, 158). It is said to form a useful, though somewhat expensive, pigment for india-rubber (Gummi Zeit. 1903, 17, 418).

Phosphomolybdic acid $H_3PO_4,12MoO_3$ is formed by treating its ammonium salt with *aqua regia* (Finkener, Ber. 1878, 11, 1638; Kehrmann, Ber. 20, 1811; Levi and Spelta, Gazz. chim. ital. 1903, 33, i. 207; Miolati, *ibid.* ii. 335) is employed as a reagent for alkaloids. Its ammonium salt is a canary-yellow crystalline powder almost insoluble in water and in dilute acids consisting of a variable mixture of di- and tri-ammonium phosphomolybdates, according to the composition of the ammonium molybdate solution used (Posternak, Compt. rend. 1920, 930).

Permolybdic acid $H_2MoO_5xH_2O$ is an orange-red amorphous powder, formed by treating the trioxide with hydrogen peroxide (Muthmann and Nagel, *l.c.* 1836); a number of permolybdates have been prepared.

Sulphides. *Molybdenum sesquisulphide* Mo_2S_3 forms steel-grey needles of sp gr. 5·9 at 15°, and is obtained by heating the disulphide in the electric furnace (Guichard, Compt. rend. 1900, 130, 137).

Molybdenum disulphide MoS_2 occurs native as *molybdenite* in foliated scales or in tabular hexagonal prisms, and can be obtained artificially by fusing the trioxide with sulphur or by heating it in sulphuretted hydrogen. It is very similar to graphite in appearance, possessing a metallic lustre and a lead-grey colour, but it is incombustible in the blowpipe. It is oxidised with evolution of sulphur dioxide when heated in the air, and when treated with nitric acid or *aqua regia*.

Molybdenum trisulphide MoS_3, obtained by the action of sulphuretted hydrogen on a concentrated molybdate solution, is a black-brown powder, which combines with basic sulphides to form thiomolybdenum salts (Annalen, 1884, 225, 1; Hofmann, Zeitsch. anorg. Chem. 1896, 12, 55). Molybdenum tetra-sulphide and thiomolybdic acids are also known.

Halides and other compounds. Molybdenum forms a large number of halogen, mixed and double halogen, and oxyhalogen salts (Muthmann and Nagel, *l.c.*; Guichard, Compt. rend. 1896, 123, 821; Bull. Soc. chim. 1901, [iii.] 25, 188; Klason, *l.c.* 148; Nordenskjold, Ber. 1901, 34, 1572; Ruff and Eisner, *ibid.* 1907, 40, 2926, 3931; Rosenheim and Kohn, Zeitsch. anorg. chem. 1910, 66, 1: Koppel, *ibid.* 1912, 77, 289). Molybdenum combines with silicon to form silicides (Vigouroux, Compt. rend. 1899, 129, 1238; Defacqz, *ibid.* 1907, 144, 1424; Bull. Soc. chim. 1908, [iv.] 3577; Watts, Trans. Electro. J. 1906, 9, 105; Hönigschmid, Monatsh. 1907, 28, 1017); with boron to form borides (Tucker and Moody, Chem. Soc. Trans. 1902, 16; Binet du Jassonneix, Compt. rend. 1906, 143, 169); with carbon to form carbides (Moissan and Hoffmann, *ibid.* 1904, 138, 1558); and with carbon monoxide, forming a carbonyl compound (Mond, Chem. Soc. Trans. 1910, 798; Mond and Wallis, *idem.* 1922, 29).

Molybdenum cyanides and thiocyanates and their complex salts with a number of organic compounds have been prepared (Rosenheim, Zeitsch. anorg. Chem. 1906, 49, 148; *ibid.* 1907, 54, 97; *ibid.* 1910, 66, 95; Ber. 1915, 48, 1167; Ber. 1908, 41, 2386; *ibid.* 1909, 42, 149, 2295; Sand and Maas, *ibid.* 1907, 40, 4504; *ibid.* 1908, 41, 1500, 1861, 3367; *ibid.* 1909, 42, 2642; Chilesotti, Gazz. chim. ital. 1904, 34, ii. 493; Olsson, Ber. 1914, 47, 917). A number of salts of molybdenum with organic acids have also been prepared (Rosenheim, Ber. 1895, 26, 1191; Zeitsch anorg Chem. 1903, 34, 427; Grossman and Kramer, *ibid.* 1904, 41, 43; Ber. 1903, 34, 1606; Henderson and Barr, Chem. Soc. Trans. 1896, 1455; Orr and Whitehead, *ibid.* 1899, 546; Mazzucchelli, Atti R. Acad. Lincei, 1909, [v.] 18, ii. 259; Mazzucchelli and Zangrilli Gazetta, 1910, 40, ii 49; Mazzucchelli and Borghi, *ibid.* 1910, 40, ii. 241)

Molybdamide $OH{\cdot}MoO_2{\cdot}NH_2$ is obtained by treating a chloroform solution of molybdic chloride with ammonia. A black precipitate of the diamide is obtained, which, when extracted with alcohol, is converted into the brownish-red amorphous monamide.

The *monoethylamide* $OH{\cdot}MoO_2\,HNEtH_2O$, a white powder and the *diethylamide*

$$MoO_2(NHEt)_2,$$

a reddish-brown powder are formed readily by the action of molybdenum chloride on ethylamine. The diamide reacts violently with nitric acid, and gives a deep blue solution with strong sulphuric acid (Fleck and Smith, Zeitsch anorg. Chem. 1894, 7, 351).

Molybdenum tannate is of a deep yellow colour, soluble, and has a great affinity for vegetable fibre. It produces fast shades on leather, and in conjunction with logwood extracts a variety of shades may be obtained (Pozzi-Escot, Compt. rend. 1902, 135, 880).

Nicotine ammonium molybdate, prepared by the action of ammonium molybdate on nicotine in the presence of acetic acid is a white powder, sp.gr. 2·5407, and is intensely poisonous. On oxidation in acid solution it yields nicotinic acid, but in alkaline solution dipyridine is formed (Meszlényi, Landw. Versuchs.-Stat., 1905, 61, 321).

Gerber (Mon. Scient. [v.] 7, 73, 83, 121–127, 169–171, 219–227, 1917) finds evidence of a new element associated with molybdenum, which he terms *neomolybdenum*, of atomic weight 99 which is spectroscopically indistinguishable from molybdenum and, it is surmised, may be an isotope of that element.

MOLYBDITE or **MOLYBDIC-OCHRE.** This mineral, long thought to be molybdenum trioxide MoO_3, has been proved by W. T. Schaller (1907) to be really a hydrated ferric molybdate, $Fe_2O_3{\cdot}3MoO_3{\cdot}7\frac{1}{2}H_2O$, or perhaps with $7H_2O$. Being a secondary mineral usually intimately associated with limonite, the iron, when detected,[1] had previously been regarded as an impurity. It occurs in sparing amounts as pale yellow, earthy or powdery encrustations, and is sometimes crystallised as tufts of short silky fibres. These fibres are strongly birefringent with straight extinction; the pleochroism is strong with marked absorption (pale yellow for vibrations across the fibres, and deep yellow to almost black for vibrations parallel to their length). The mineral has been formed by the oxidation (weathering) of molybdenite (MoS_2), with which it is usually to be found. It is thus quite distinct from the artificial molybdenum trioxide, which has a platy structure, and is colourless and non-pleochroic. The existence of the latter as a mineral thus remains to be proved. Meanwhile, the name *ferrimolybdite* (P. Pilipenko, 1914) has been suggested for the iron molybdate mineral. L. J. S.

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[1] An iron molybdate had, in fact, been described from California in 1852, and from Georgia by W. J. Taylor in 1855.

MOMORDICA FAT. A fat obtained from the kernels of the seeds of *Momordica cochinchinensis*, a cucurbitaceous plant found in Bengal, the Philippine Islands, &c., by extraction with petroleum spirit, or by pressure at 40°. The fat consists chiefly of glycerides of fatty acids and no wax alcohols are present. On exposure to the air the fat gradually becomes yellow and granular and on heating to 220°–240° changes to a greenish-brown liquid which remains liquid and has the consistency of castor oil. When freshly prepared m.p. is 28°–32°, refr. index (40°) 1·495, acid value 1·9, sapon. value 185·2, iodine value 23·4. The fatty acids melt at 46°–51°; solidification point 44°–42°; neutralisation value 188·3; iodine value about 40° (Corfield and Caird, Pharm. J. 1920, 104, 43).

MOMORDICINE. Syn. for ELATERIN. *See* ELATERIUM.

MONARSONE. Di-sodiumethyl-arsonate. Suggested as a substitute for salvarsan, as less toxic, freely soluble, and without hæmolytic action.

MONAZITE. A mineral consisting essentially of phosphate of the cerium metals $(Ce,La,Di)PO_4$, crystallising in the monoclinic system. Several other elements (yttrium, silicon, iron, calcium, tin, &c.) are usually present in small amounts, and in particular thorium (ThO_2 1–11 p.c., rarely as high as 28 p.c.). Few minerals have had a more romantic history. It was named by A. Breithaupt in 1829 from *μονάζειν*, to be solitary, on account of the rarity of the singly-occurring crystals from the Ural Mountains; but it has since been found to be widely distributed, and in certain places to be accumulated in large quantities. Small brilliant crystals, often mistaken for sphene or anatase, had been earlier known from the gneissic rocks of the Alps. These were named turnerite by A. Lévy in 1823, but being of unknown composition their identity with monazite was not established until long afterwards. They were described as coming from 'Mont Sorel' in Dauphiné, a statement due to the misreading of a label 'Pictite [=sphene] de Mons. Soret, Dauphiné' (H. A. Miers, Min. Mag., 1889, 8, 207). The shipping of sand as ballast from the Brazilian coast led to the discovery of extensive deposits of monazite sand. This material had, however, no commercial value until the introduction of incandescent gas-lighting. For this purpose it is mainly the accessory and variable constituent thoria that is required, and for a time the larger quantities of cerium and didymium earths were practically waste products. These have now found important applications. The former for making the cerium-iron alloys (pyrophoric alloy or sparking metal) used in automatic lighters; whilst the didymium salts are employed in the manufacture of marking inks and dyes. Another by-product—the phosphoric acid—could perhaps be utilised as a garden fertiliser. Finally, in working the deposits of this mineral there have always been the German monopolies to contend against.

Crystals of monazite are yellowish-brown and translucent, or dull brown and opaque, with a lustre inclining to resinous. Sp.gr. 4·9–5·3; hardness 5½. Monazite gives the absorption spectrum characteristic of didymium salts, and this affords a ready means of detecting the mineral with the aid of a pocket spectroscope or a spectroscopic attachment to the microscope. Dull crystals of monazite of fair size are found in the pegmatite-veins of the Ilmen mountains in the southern Urals, and at several places in the south of Norway. A sharply developed isolated crystal from Tvedestrand, Norway, in the mineral collection of the British Museum, weighs 1½ kg. As small grains embedded in gneissic and granitic rocks monazite has a very wide distribution, though only in relatively very small amounts (O. A. Derby, Min. Mag., 1897, 11, 304). With the weathering and breaking down of such rocks, the monazite is accumulated with the other heavy minerals in the beds of streams. Under these circumstances it is often met with in alluvial gold washings. The minute grains (0·1–1 mm. diam.) are always well rounded, owing to the comparative softness of the mineral; and are associated with grains of magnetite, ilmenite, chromite, garnet, zircon, rutile, &c. The careful examination of the heavy residues of river sands rarely fails to reveal the presence of some grains of this mineral. Occurrences of this kind have been recorded from all parts of the world, but it is only in Brazil, North and South Carolina, Travancore, and perhaps Ceylon, that the deposits are sufficiently rich to be worked commercially. The several minerals present in these sands have a wide range in their magnetic permeability, monazite itself being weakly magnetic, and they can be separated by means of a series of electro-magnets of different strengths.

The following are selected from a series of twenty analyses by S. J. Johnstone (J. Soc. Chem. Ind. 1914, 33, 55) of monazite isolated from sands, from: I. Travancore, II. Ceylon, III. Pahang, IV. Northern Nigeria, V. Nyasaland, and VI. Brazil.

	I	II	III	IV	V	VI
ThO_2	10·22	10·75	8·38	5·00	7·10	6·06
Ce_2O_3	31·90	26·71	25·46	30·72	32·52	62·12
La_2O_3, &c.	28·00	30·06	32·72	30·02	26·91	
Y_2O_3, &c.	0·46	1·46	2·80	2·74	1·50	0·80
Fe_2O_3	1·50	1·09	0·84	3·00	1·10	0·97
Al_2O_3	0·17	0·70	2·78	0·35	0·20	0·10
CaO	0·20	0·85	0·61	0·15	0·32	0·21
SiO_2	0·90	2·47	0·92	1·20	1·66	0·75
P_2O_5	26·82	24·61	23·92	26·29	28·16	28·50
Ign.	0·46	0·93	1·28	0·25	0·25	0·38

The mineral is soluble with difficulty in hydrochloric acid, but is decomposed by sulphuric acid. S. L. Penfield (1882) believed the thorium to be present as mechanically admixed thorite, since the ratio $SiO_2 : ThO_2$ often approximates to unity. Later analyses of crystals do not, however, support this view.

In Brazil, monazite-bearing sands are found on the sea-shore at certain spots near Alcobaca and Prado in the south of the State of Bahia, and at various points along the coast of the States of Espirito Santo and Rio de Janeiro. The amount exported annually is about 5000 tons. In the Carolinas, alluvial deposits are worked in the valleys of the several streams draining the South Mountains, an eastern outlier of the Blue Ridge. These sands contain monazite in amounts reaching 1–2 p.c., and they are concentrated by the washing methods of the gold miner. Magnetite and other ferriferous minerals are extracted by a magnet, and the product contains 65–70 p.c. of monazite mixed with other heavy minerals, such as zircon, garnet, rutile, corundum, &c. This cleaned monazite-sand is fine in grain, and of a resinous yellow colour with darker specks of other minerals. The production amounts to about 200 tons per annum, but it is now decreasing. Near Mars Hill in Madison Co., North Carolina, masses of monazite up to 60 lbs. in weight have been found in pegmatite; and in the mica mines at Villeneuve in Quebec masses of 20 lbs. have been met with. At the felspar quarries of the south of Norway the isolated crystals of monazite are picked out by hand, about a ton per annum being so collected. The deposits discovered in 1909 in Travancore occur along the sea-shore at certain spots between Quilon and Cape Comorin on the extreme south-west coast of India. The mineral is also present in the sand-dunes on the coast, and in many of the rivers and streams; and it has been detected in the gneisses and pegmatites of the adjoining country, being there often associated with graphite.

References.—H. B. C. Nitze, 16th Ann. Rep. U. S. Geol. Survey, 1895, pt. iv 667–693; W. T. Schaller, Mineral Resources, U S. Geol. Survey (for 1916), 1917, 2, 223; K. L. Kithil, U.S. Bureau of Mines, 1915, Techn. Paper, No. 110; G. P. Merrill, The Non-metallic Minerals, 2nd ed. 1910; S. I. Levy, The Rare Earths, London, 1915; Bull. Imperial Inst. London, 1905, 3, 151, 233, 285; Monazite, 1913–19, Imp Min. Res. Bur. London, 1920; J. H Pratt and D B. Sterrett, Monazite and Monazite-Mining in the Carolinas, Trans. Amer. Inst Mining Engin. 1910, 40, 313–340. On some of the Brazilian occurrences, *see* F. Freise, Zeitsch. prakt. Geol. 1909, 17, 514; 1910, 18, 143. On the Travancore deposits, *see* G. H. Tipper, Rec. Geol. Survey India, 1914, 44, 186; Bull. Imp. Inst., 1911, 9, 103; 1913, 11, 699; 1915, 13, 323. On those of Ceylon, Bull. Imp. Inst., 1916, 14, 321. L. J. S.

MONAZITE, ANALYSIS OF. The following account of a method of analysis of monazite is condensed from a description given by Sydney J. Johnstone, of the Scientific and Technical Department of the Imperial Institute and published in the Journal of the Society of Chemical Industry, 1914, 33, 55. The scheme embodies Glaser's oxalate method for the separation of the rare earths, Fresenius and Hintz's thiosulphate method for the separation of thoria, and Mosander's chlorine method for the separation of ceria.

One to two grams of the monazite are finely ground, the loss on ignition determined, and the residue digested with 5 c.c. of concentrated sulphuric acid for 2 to 3 hours. After cooling the syrupy mixture of sulphates is poured into 100 c.c. of cold water and allowed to stand for half an hour. After being filtered off and washed, the insoluble residue is again digested with sulphuric acid, washed, ignited and weighed. The silica in this residue is estimated by evaporation with hydrofluoric and sulphuric acids and the residue remaining, which rarely exceeds 0·1 p.c., is examined separately for bases.

Total rare earths. The combined sulphuric acid filtrates are made up to about 600 c.c., nearly neutralised with ammonia, acidified with about 10 c.c. of hydrochloric acid and the rare earths precipitated by ammonium oxalate. After standing for 12 hours the rare earth oxalates are filtered off, ignited, re-dissolved, re-precipitated, and after standing, again filtered and well washed with a 1 p.c. solution of ammonium oxalate acidified with hydrochloric acid. The precipitate after ignition is weighed as 'total rare earths.'

The filtrates from the oxalate precipitation are examined for traces of rare earths, by evaporation nearly to dryness with nitric acid, solution of the residue in hydrochloric acid and precipitation in small bulk with ammonium oxalate. Any rare earths found are re-precipitated and added to the quantity found above.

Iron, aluminium, calcium, and phosphoric acid. The filtrate from the precipitations with ammonium oxalate is treated by Glaser's method (*v. supra*).

Thoria. The 'total rare earth' oxides are dissolved in hydrochloric acid, the solution diluted to 200 c.c. and heated to boiling; it is then nearly neutralised with ammonia, about 5 grams of sodium thiosulphate added, and boiled for half an hour. After standing at a temperature just below boiling for 8 to 10 hours, the precipitated basic thorium thiosulphate is filtered off, washed, dissolved in strong hydrochloric acid, and after nearly neutralising, re-precipitated by sodium thiosulphate. This precipitate is dissolved in hydrochloric acid and after filtering from the sulphur is precipitated as oxalate and weighed as thoria (ThO_2). In order to recover the small amount of thoria which sometimes passes into the thiosulphate filtrate it is necessary to evaporate the solution with nitric acid. The rare earths are then precipitated as hydroxides, dissolved in hydrochloric acid and again treated with sodium thiosulphate, the thoria obtained being added to that already found.

Yttrium earths. The total thiosulphate filtrates are evaporated to a small bulk and the thiosulphate destroyed by nitric acid as before. The solution is evaporated to dryness, the residue dissolved in 10 c.c. of hydrochloric acid, diluted, and the remaining rare earths precipitated as oxalates. The precipitate is carefully washed free from sulphates, ignited, dissolved in concentrated hydrochloric acid and evaporated to dryness on the water-bath. The residue so obtained is dissolved in 5 c.c. of water and about 200 c.c. of a saturated solution of potassium sulphate added, together with 5 grms. of finely powdered solid potassium sulphate. After standing for 12 hours, with occasional agitation, the precipitate of double sulphates of potassium with the cerium and lanthanum earths is filtered from the soluble yttrium earth sulphates and washed with a saturated solution of potassium sulphate. This precipitation is repeated on the insoluble sulphates. The yttrium earths in the combined filtrates are precipitated by a slight excess of ammonia, filtered, re-dissolved in hydrochloric acid, precipitated as oxalates and weighed as yttrium earth oxides (Y_2O_3, &c.).

Ceria, lanthana, &c. The precipitated double sulphates obtained as above described are transferred, with the filter paper, to a beaker and boiled with 400 c.c. of water and 5 c.c. of hydrochloric acid until dissolved. The separation of the ceria from the other rare earth oxides present is effected by the following modification of Mosander's method. The earths are precipitated by ammonia, filtered, washed, dissolved in hydrochloric acid and the solution diluted to about 200 c.c. The solution is neutralised with potassium hydroxide, and about 2 grams excess added. A current of chlorine is passed through the solution until the cerium is converted into the hydrated peroxide and the lanthanum and allied earths have passed into the solution, which then reacts acid. The solution, containing an excess of chlorine, is diluted to 400 c.c., allowed to stand for several hours and filtered. After washing, the precipitate is re-dissolved, the potassium hydroxide and chlorine treatment repeated twice and the cerium finally precipitated as oxalate and weighed as the oxide CeO_2.

The filtrates, containing the remaining rare earths, are evaporated to a small bulk with hydrochloric acid and the lanthanum and didymium earths precipitated as oxalates. The precipitate after filtration is decomposed with nitric acid, the earths re-precipitated as oxalates, and after ignition weighed as the oxides, La_2O_3, &c.

Phosphoric acid. The phosphoric acid can be determined in the residue remaining after the removal of the rare earths, but it is found more convenient to make this determination on a separate portion of the original sample. 0·5 gram of the finely ground monazite is fused with 5 to 7 grams of potassium carbonate in a platinum crucible for about 2 hours. The 'melt' is dissolved in water, filtered, and after washing about a dozen times with 1 p.c. potassium carbonate solution the insoluble matter is ignited, again fused with potassium carbonate and the treatment repeated as long as any phosphoric acid is extracted. Usually two fusions are sufficient. The combined filtrates are acidified with nitric acid, the phosphoric acid precipitated first as ammonium phosphomolybdate and finally as magnesium ammonium phosphate and weighed as $Mg_2P_2O_7$.

MOND GAS *v.* FUEL.

MONEL METAL. An alloy of nickel and copper made from the nickel-copper ores of Ontario; contains about 27 p.c. copper, about 68 p.c. of nickel and a slight amount of iron. Combines a strength approaching that of steel with the non-corrosive qualities of copper or brass: used for roof covering, pump-rods, marine propellers, &c. The structure of monel metal is that of a solid solution, the rolled bar, showing sharply defined crystal grains, usually twined. Mechanical tests on the rolled rod show a tensile strength of 39·2 tons; elongation of 2 in 38·5 p.c.; reduction in area 66·9 p.c. Brinell hardness, 174. The cast metal has a tensile strength of 82,500 lbs. per square inch. Elastic limit 37,500 lbs. per square inch, and elongation 44 p.c. The modulus of elasticity is from 22,000,000 to 23,000,000 lbs. as against 30,000,000 lbs. for steel and 13,000,000 lbs. for manganese bronze; m.p. 1360°, sp.gr. (cast) 8·87. Electrical conductivity 4 (copper 100). An important characteristic is the retention of the mechanical properties at high temperatures, which has led to the adoption of the alloy for locomotive fire-boxes in Germany (J. E. Thompson, Eng. and Min. J. 1911, 91, 223; J. Soc. Chem. Ind. 1911, 30, 287).

At 500° a temperature at which naval and manganese brass have no mechanical strength, the tensile strength is nearly 29 tons per sq. in. Casting of the metal is rendered difficult by the high melting point (about 1360°) and the excessive shrinkage (Arnott, J. Soc. Chem. Ind. 1918, 703 A.). *V.* NICKEL.

Analyses (Games, G. Ind. Eng. Chem. 1912, 4, 354):

——	Cast metal	Rolled metal	Forged metal
Copper .	26·59–27·53	24·76–26·99	26·69–26·83
Nickel	68·10–68·50	68·48–69·83	69·45–69·54
Iron	2·16–3·33	2·07–2·44	2·13–2·19
Carbon	0·25–0·43	0·28–0·41	0·17–0·19
Silicon	1·08–1·41	0·12–0·37	—
Manganese	0·11–0·19	1·26–1·82	1·38–1·50

The strength and other physical properties of the alloy are affected chiefly by the heat treatment rather than by slight variations in the proportion of the constituents.

MONOBROMO-CAMPHOR *v.* CAMPHORS.

MONOTAH. Trade *name* for guaiacol methyl glycollate.

MONTAN or **MONTANA WAX** is a bituminous substance extracted by various solvents from *pyropissite*, obtained from the lignites of Saxony and Thuringia, best at high temperatures (250°–260°) and pressures (50–60 atmos.). The crude substance is hard and odourless, resembling ozokerite in appearance, and having m.p. 76°–90°. Montan wax comes into commerce as a white, high-melting candle-like material. It is not a paraffin, but consists of *montanic acid* $C_{28}H_{56}O_2$, m.p. 86·5° (Meyer and Brod), 82·5° (Easterfield and Taylor), 83° (Ryan and Dillon), 83·5° (Pschorr and Pfaff), and an alcohol, m.p. 60° (*v.* Boyen, Zeitsch. angew. Chem. 1901, 14, 1110; *cf.* Marcusson, Chem. Rev. Fett.- u. Harz. Ind. 1908, 15, 193; Eisenreich, *ibid.* 1909, 16, 211; Pschorr and Pfaff, Ber. 1920, 53, 2147). Asher (D. R. P. 207488 of 1907) purifies the crude substance by heating twice with nitric acid of sp.gr. 1·2–1·4, then washing and melting it, whereby the asphaltic or resinous matter separates out. It may also be purified by dissolving in a suitable organic solvent and then heating with alcoholic alkali. After separation of the saponified matter, the wax is finally treated with concentrated sulphuric acid at 100° (D. R. P. 220050 of 1906). According to Tropsch and Kreutzer, what was thought to be pure montanic acid can be separated by esterification with methyl alcohol into two esters boiling at 265°–267·5°, and 277·5°–280° at 5 mm. pressure, respectively. From each fraction the acid was again isolated. The former has the formula $C_{27}H_{54}O_2$ and is termed *carboceric acid*, m.p. 82°; the latter is pure *montanic acid*, $C_{29}H_{58}O_2$, m.p. 86°–86·5°. The aluminium salts of montanic acid have been prepared for use as impregnating materials (D. R. P. 221888 of 1908). A number of its derivatives have been described by Meyer and Brod, Monatsh. 1913, 34, 1143; Easterfield and Taylor, Chem. Soc. Trans. 1911, 99, 2302; Grün and Ulbrich, Chem. Zentr. 1916, 2, 402; Tropsch and Kreutzer Brennstoff-Chemie, 1922, 3, 177. For action of ozone upon it, *see* Fischer and Tropsch, Chem. Zentr. 1919, 90, iv. 847.

Similar waxes are extracted from Irish peat, and sold under the names of *montana wax* and *montanin wax* (Ryan and Dillon, Proc. Roy. Dublin Soc. 1909, 12, 202).

MONTANIN. Trade name for a solution of hydrofluosilicic acid; used as a disinfectant.

MONTMORILLONITE. A clay mineral with the composition $H_2Al_2Si_4O_{12}+nAq$. It thus bears the same relation to the crystallised mineral pyrophyllite ($H_2Al_2Si_4O_{12}$) that halloysite does to the crystallised kaolinite ($H_4Al_2Si_2O_9$). It is a soft, soapy substance, softening in water, but not plastic, and it does not adhere to the tongue. Sp. gr. 2·04. The colour is white, grey, greenish, or very often pink. It occurs as an alteration product in sedimentary rocks, in mineral veins, and in igneous rocks. Analysis by L. Azéma (1913) of rose pink material from Bordes near Montmorillon (the original locality) in Dep. Vienne, France, gave (also traces of CoO, MnO, NiO):

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	H_2O
59·57	22·83	1·07	3·82	2·21	10·46

There are several varieties distinguished by special names. L. J. S.

MOONSTONE *v.* FELSPAR.

MORAVITE *v.* THURINGITE.

MORDANT ROUGE. *Aluminium acetate v.* ACETIC ACID.

MORIN *v.* OLD FUSTIC.

MORINDA CITRIFOLIA. The roots of *Morinda citrifolia* (Linn.) and *Morinda tinctoria* (Roxb.), known as 'Morinda Root,' are extensively employed in various parts of India under the general trade name of *Suranji*, more especially for dyeing reds, purples, and chocolates. These plants, the native names for which are *Aal*, *A'l*, *Ach*, or *Aich*, are to be met with in nearly all the provinces of India, either wild as in the jungles of Bengal, or cultivated in small patches in betelnut plantations, or near the homesteads of the dyers. In Bengal the plant is usually propagated by slips or cuttings, but in other parts it is raised from seed, as well as from cuttings. When the plants have attained a height of from 5-6 feet, that is, as a rule, about the end of the third year, the straight spindle-shaped roots which extend into the ground to the depth of 3 or 4 feet, are dug out and the upper portions of the plant are cut into slips to serve for the propagation of the next crop.

The colouring matter is found principally in the root bark, and is developed in greatest quantity at about the end of three or four years, depending upon the character of the soil. After this time the dyeing principle gradually disappears, and the matured trees, which eventually attain the height of a mango tree, contain hardly a trace of it. The thin roots are most valuable, roots thicker than half an inch being thrown away as worthless. They are or were mainly used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but they are also employed for dyeing the coarse cotton fabric called 'Khárva,' or for dyeing the silk thread which forms the border of the silk fabric known as 'Endi cloth.' The colours given by A'l range from a reddish-yellow through pink and various shades of red to a dark brown-red. The tint seems to depend primarily upon the age of the root, and upon the proportion of root bark to stem which is employed. The root bark gives the best reds; the dye in the woody part of the root is yellow, and hence when the wood preponderates over the bark the resulting dye is reddish-yellow.

About 1790 some of the powdered root under the name of 'aurtch' came into the hands of Dr. Bancroft, who found little or no difficulty in applying it to both wool and cotton. At that time he considered that it might be profitably imported into Europe.

In 1832 Schwartz and Koechlin also examined the root under the names "Nona' and 'Hachrout,' and reported on its dyeing properties to the Industrial Society of Mulhouse. They referred to the fact that of all the Indian *rubiaceæ* examined by them, it contained the largest quantity of certain yellow principles of an acid character which not only necessitated the washing of the root with cold water before dyeing, but also made it requisite to add a certain proportion of sodium carbonate to the dye-bath in order to have a perfectly neutral bath. Their conclusion was that since morinda root only possessed one-third the dyeing power of a medium quality of madder, it could never compete with the latter in the European market.

About 1848 some morinda root was submitted for trial to some of the most experienced and skilful calico printers of the Glasgow district, all of whom concurred in declaring it not to be a dye at all.

In 1848 Anderson (Annalen, 71, 216) isolated from the root of the *Morinda citrifolia* by extraction with alcohol, a crystalline yellow substance which he named *Morindin*, and to which he assigned the formula $C_{28}H_{30}O_{15}$. This substance when strongly heated, gave a crystalline sublimate *morindon*, and Anderson pointed out the great similarity, on the one hand, between morindin and ruberythric acid, and on the other between morindon and alizarin.

Rochleder (Annalen, 1852, 82, 205) gave it as his opinion that morindin and morindon were identical with the ruberythric acid and alizarin derived from madder, and Stokes (Chem. Soc. Trans. 2, [2] 333), by examining the absorption spectra of solutions of alizarin and morindon in sodium carbonate and in ether, came also to the conclusion that these two colouring matters consisted of one and the same substance. Stenhouse (J. 1864, 17, 543) formed a similar opinion, and pointed out that morindin not only gives morindon by heating, but also when digested with boiling dilute mineral acids.

On the other hand, Stein (J. 1866, 19, 645) found that the absorption spectra of alizarin and morindon are not identical, and that ruberythric acid and morindin are distinct substances, although the latter resemble each other in the respect that both are glucosides. The distinction between these compounds was rendered much clearer by the work of Thorpe and Greenall (Chem. Soc. Trans. 1887, 51, 52), and Thorpe and Smith (*ibid.* 1888, 53, 171), who showed that morindon possesses the formula $C_{15}H_{10}O_5$; on distillation with zinc-dust it gave methylanthracene (m.p. 190°–191°), and was evidently a derivative of methylanthraquinone. To morindin, the glucoside, the formula $C_{26}H_{28}O_{14}$ was assigned

Somewhat later Perkin and Hummel (Chem. Soc Trans. 65, 851), during an examination of the *Morinda umbellata* (Linn) (*v infra*), proved that morindon contains three hydroxyl groups, and that Thorpe and Smith's hydrocarbon was β-methylanthracene.

Oesterle and Tisza (Arch. Pharm. 1907, 245, 531) consider that the true formula of morindin is $C_{27}H_{30}O_{15}$, and that its hydrolysis with acid can be expressed as follows:—

$$C_{27}H_{30}O_{15}+2H_2O=2C_6H_{12}O_6+C_{15}H_{10}O_5$$

The sugar thus formed is not fermented by yeast and yields an osazone melting at 197°.[1]

Morindin crystallises from 70 p.c. alcohol in glistening yellow needles, which melt at 245°, and dissolve in alkaline solutions with a red colour. It does not dye mordanted fabrics

Nono-acetylmorindin $C_{27}H_{21}O_{15}(COCH_3)_9$ (O and T.), citron yellow needles, melts at 236° (?).

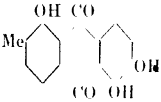
Nono-benzoylmorindin $C_{27}H_{21}O_{15}(CO\,C_6H_5)_9$ (O. and T.), yellow needles, melts at 186°.

Morindon, the colouring matter of *Morinda citrifolia*, which is obtained by the hydrolysis of morindin, and also exists as a rule to some extent in the free state in this root, consists of orange-red needles, melting at 271°–272°. It is soluble in alkaline liquids, with a blue-violet tint, somewhat bluer than the corresponding alizarin solutions, which, when treated with baryta water, give a cobalt-blue precipitate of the barium derivative. Its solution in sulphuric acid is blue-violet.

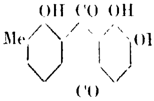
Triacetylmorindon $C_{15}H_7O_5(COCH_3)_3$ crystallises in citron-yellow needles, melting at 242°.

Morindon trimethylether $C_{15}H_7O_2(OCH_3)_3$ is a yellow crystalline powder, melting at 229°.

Simonsen (Chem. Soc. Trans. 1918, 113, 766) has thrown more light on the constitution of morindon, which was known to yield 2-methylanthracene on distillation with zinc-dust and believed to be a trihydroxymethylanthraquinone (Perkin and Hummel, Chem. Soc. Trans. 1894, 65, 851). This view has now been confirmed, and it is found further, that two of the hydroxy groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yielded a monomethyl ether, whilst two of the hydroxyl groups are probably in the 1 : 2-position, since morindon is a mordant dye resembling alizarin. These and other reasons lead to the belief that it has one of the two formulæ given, (I.) being thought the more probable



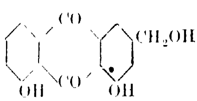
(I.)



(II.)

(C S. Reports, 1918, 86).

The exact constitution of morindon has not yet been determined, but it appears probable that if this compound contains in reality three phenolic hydroxyls, it most likely consists of a methyl anthragallol. If, on the other hand, as is quite probable, morindon contains an alcoholic group, which, according to Robinson and Simonsen, occurs in the isomeric aloe-emodin—



then its constitution will be represented as alizarin in which one of the three β-positions is occupied by CH_2OH. Though such a constitution would appear to harmonise well with the present known properties of morindin, according to Simonsen (private communication) experimental evidence of a CH_2OH group in this compound is lacking.

In many respects the *Morinda citrifolia* resembles chay root and madder, for, in addition to morindin and morindon, it contains a large quantity of *chlorogenin*, and certain yellow non-tinctorial substances, derivatives of anthraquinone. The preparation of morindon in quantity can be conveniently carried out by extraction with sulphurous acid, according to the details given in the sections on Madder and Chay Root for the isolation of natural alizarin. Simonsen (Chem. Soc. Trans 1920, 117, 561) has investigated the residue remaining after extraction of morindin, and has isolated alizarin-α-methyl ether and rubiadin mono-methyl ether, the former being identical with that obtained by Perkin and Hummel from the Oldenlandia umbellata (*see* CHAY ROOT) and the latter with the substance obtained by Barrowcliff and Tutin (see later) from M. longiflora

From the alcoholic extract of the *Morinda citrifolia*, Oesterle (Arch. Pharm. 1907, 245, 287) has isolated a small quantity of a substance which has the constitution of a *monomethyl ether* of a *trihydroxymethylanthraquinone*. It consists of yellow crystals, melting at 216°, soluble in hot alkaline solutions, with a yellowish-red colour. It is not, as this author suggested, identical with the emodin methyl ether which exists in the *Ventilago madraspatana* (A. G. Perkin, Chem. Soc. Trans. 1907, 2074).

Dyeing properties.—In Dr. G. Watts' Dictionary of the Economic Products of India, Dr. J. Murray has written under the head of *Morinda*, not only a most complete account of the more important species, but full details of the native methods of dyeing with them. These methods of dyeing vary considerably in different parts of India, but they are all similar in general principles, and are practically crude processes of the turkey-red dyeing known in Europe. An extended series of dyeing experiments in connection with morinda root have been carried out by Hummel and Perkin (J. Soc. Chem. Ind. 1894, 13, 346), who find that by adopting certain precautions this dyestuff possesses a dyeing power which is greater than madder itself.

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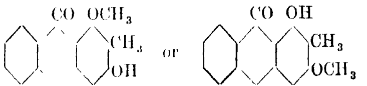
[1] Simonsen (private communication in 1918) considers this to be incorrect, and that the formula $C_{26}H_{28}O_{14}$ of Thorpe, Greenall and Smith (cf. Perkin, Chem. Soc. Proc. 1908, 24, 149) correctly represents morindon. *See also M. umbellata.*

To obtain good results it is necessary, as previously indicated by the work of Schwartz and Koechlin (*l.c.*), to neutralise, or better still to remove, the free acid which exists in considerable quantity in the roots. Experiments also with the powdered morinda root which had been allowed to ferment, or had been digested with boiling dilute acid, as in the preparation of 'garancine' from madder, showed that these preparations dyed exceedingly well when 1 p.c. of chalk was added to the dye-bath. It was found, for instance, that 7·5 grams of a sample of washed morinda root (equivalent to 10 grams of the unwashed root) had a dyeing power equal to 15 grams madder root of good quality.

The reds and pinks obtained on alumina mordant are yellower than the corresponding madder colours, the chocolate presents a similar difference in tone, and hence again appears fuller than a madder chocolate, whilst the lilac is distinctly redder. Oil-prepared calico mordanted as for turkey-red gives a very bright orange-red or scarlet similar in shade to that given by flavopurpurin, and fast to clearing with soap and stannous chloride. Chromium mordant on similarly prepared calico gives a full rich chocolate, and iron mordant yields colours varying from dull purple to black, according to the intensity of the mordant. On wool and silk, mordanted according to the usual methods, good chocolate-browns are obtained with chromium, orange-reds with alumina, bright orange with tin, and dark purple and black with iron mordant. All the colours referred to are as fast to soap as the corresponding madder colours. With respect to wool and silk in the unmordanted condition, these fibres may be readily dyed both with the washed and unwashed root, more or less rich orange or yellow colours, the brightness of which is enhanced by the addition of a little acetic acid to the dye-bath. These colours, however, which appear to originate from the glucoside morindin itself, are of a sensitive character towards alkalis and of little value. A. G. P.

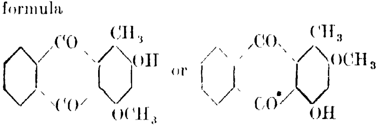
MORINDA LONGIFLORA. *Morinda longiflora*, known as 'Ojuologbo' (woody vine) (Jour Soc. of Arts, 1905, 53, 1069), is a native of West Africa, and considered to be one of the most valuable medicinal plants of that region. It is fully described in the Flora of Tropical Africa (1877, 111, 192), where it is stated to be known under the native name of 'Mibogga.'

According to Barrowcliff and Tutin (Chem. Soc. Trans. 1907, 91, 1909) the root of the *Morinda longiflora* (G. Don) contains an *hydroxymethoxymethylanthraquinone* and an *alizarin-monomethyl ether*, although morindin, the common constituent of the roots of the *Morinda citrifolia*, *Morinda tinctoria*, and *Morinda umbellata*, is absent. The hydroxymethoxymethylanthraquinone $C_{16}H_{12}O_4$, yellow needles, melts at 290°, and the acetyl derivative at 173°. Heated with 70 per cent. sulphuric acid it gives the 1 : 3-dihydroxy-2-methylanthraquinone of Schunck and Marchlewski (Chem. Soc. Trans. 1894, 65, 182). Accordingly it possesses one of the following formula—



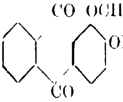
Hydriodic acid converts it into dihydroxymethylanthranol $C_{15}H_{12}O_3$ (m.p. 235°), and by methylation 1 : 3-dimethoxy-2-methyl anthraquinone (m.p. 181°) is produced.

Simonsen (Chem. Soc. Trans. 1920, 117, 561), however, states that Barrowcliff and Tutin's compound is not derived from 1 : 3-dihydroxy-2-methylanthraquinone for the dihydroxymethylanthraquinone obtained on hydrolysis gives an acetyl derivative, m.p. 225°, whereas the 1 : 3-dihydroxy-2-methylanthraquinone of Schunck and Marchlewski has an acetyl derivative, m.p. 217–218°. It is evidently the monomethyl ether of rubiadin and possesses the formula



The so-called 1 : 3-dimethoxy-2-methylanthraquinone is thus *rubiadin dimethyl ether* (1 : 3-dimethoxy-4-methylanthraquinone).

The monomethyl ether of alizarin



is identical with the compound isolated by Perkin and Hummel (Chem. Soc. Trans. 1893, 63, 1174) from chay root, *Oldenlandia umbellata* (Linn.).

The leaves of the *Morinda longiflora* also contain the above-mentioned hydroxymethoxymethylanthraquinone, and in addition a crystalline alcohol *morindanol* $C_{38}H_{62}O_4$, which melts at 278° and has $[\alpha]_D + 65{\cdot}9°$. With sodium methoxide and methyl iodide it yields methyl morindanol $C_{33}H_{61}O_3{\cdot}OCH_3$ (m.p. 116°).

'Ojuologbo' does not appear to contain an alkaloid, and extracts of the leaves and root were not found to possess any pronounced physiological action (B. and T.). A. G. P.

MORINDA UMBELLATA OR MANG-KOUDU. The dyeing material, variously named oungkoudou, jong-koutong, &c., is the root-bark of *Morinda umbellata* (Linn.), and is met with in Eastern commerce in the form of small, reddish-brown, irregular rolls of bark, much wrinkled in appearance. Its cost is or was about 6*d.* per lb. In Java it is largely used for producing the fast reds in the native calico prints, well known under the name of 'baticks.'

Although the shrub from which the root-bark is obtained is met with in Ceylon and the hilly regions of Eastern, Southern, and South-Western India, as well as in the Malay Peninsula and Java, the material does not appear to be considered as of any special importance by the Hindoo dyers, unless, indeed, as is very probable, they use the root as a whole under the general designation 'ál root,' of which it must simply be regarded as a variety.

The following are a few of its Indian vernacular names: Al (Bomb); núna (Tamil); múlúghúdú (Telugu); mang-koudu (Malay).

The older literature connected with mang-koudu is extremely limited, brief reference to its dyeing properties only being found in the following publications: Philosophy of Permanent Colours (1813), Bancroft; Bulletin de la Société Industrielle de Mulhouse (1832), E. Schwartz and D. Koechlin; L'Art de la Teinture des Laines (1849), Gonfreville, Monograph on the Dyestuffs and Tanning Matters of India, &c. (1878), T. Wardle; Watt's Dictionary of the Economic Products of India (1891), J. Murray.

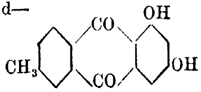
The examination of this dyestuff by Perkin and Hummel (Chem Soc. Trans. 65, 851) has indicated its close chemical resemblance to the *Morinda citrifolia*. It contains a glucoside of the nature of morindin, which yields by hydrolysis morindon, but which, according to Perkin (Chem. Soc. Proc. 1908, 24, 149), is best represented by the formula $C_{26}H_{28}O_{14}$, and is identical with that suggested by Thorpe and Greenall (Chem. Soc. Trans 1887, 51, 52) for the morindin derived from the *Morinda citrifolia*. The *acetyl* derivative $C_{26}H_{20}O_{14}(C_2H_3O)_8$ is very sparingly soluble in alcohol, and melts at 246°–248°, and the sugar produced from the glucoside yields an osazone melting at 202°–203°, which is not readily dissolved by alcohol.

This root-bark contains a considerable quantity of chlorogenin (*cf.* MADDER), together with a small amount of non-tinctorial yellow derivatives of anthraquinone. A quantitative examination of the extract from 200 grams of the material with sulphurous acid (*cf.* MADDER) gave 9·47 grams of green precipitate, which yielded:—

Crude chlororubin	8·075	grams	=4·03 p.c.
Pure morindon .	1·187	,,	=0·59 ,,
Yellow substances	0·208	,,	=0·104 ,,

These yellow substances proved to consist of a mixture of at least six distinct compounds. The main constituent isolated in yellow needles, melting at 171°–173°, possessed the formula $C_{16}H_{12}O_5$, and had properties in harmony with those required by a monomethyl ether of a trihydroxymethylanthraquinone. The diacetyl derivative $C_{16}H_{10}O_5(C_2H_3O)_2$ melts at 148°.

A second compound, $C_{15}H_{10}O_4$, crystallised in yellow needles, melting at 269°, and was found to consist of the *methylpurpuroxanthin* prepared synthetically (Marchlewski, Chem. Soc. Trans. 1893, 63, 1142) by the condensation of metadihydroxybenzoic acid with paramethyl benzoic acid—



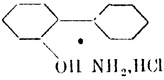
The remaining yellow substances, (*a*) $C_{16}H_{12}O_6$, orange-red needles, m p. 258°, (*b*) $C_{16}H_{10}O_5$, lemon-yellow needles, m p. 198°–199,° (*c*) $C_{16}H_{10}O_5$, needles, m.p 208°, were isolated in such small amount that a determination of their constitution could not be attempted.

Dyeing properties.—This dyestuff is largely employed by the Javanese for producing the fast reds in their celebrated 'baticks.' The colours it yields are practically identical with those given by morinda root, but much fuller, a fact not to be wondered at, for it is well known that in ordinary morinda root the colouring principle is situated chiefly in the root bark. In its ordinary condition mang-koudu is not useful in dyeing, but as in the case of ál root, a preliminary washing or steeping in water suffices to remove the deleterious acid principles present, and thus to transform it into a valuable red dyestuff. A. G. P.

MORINDIN *v.* MORINDA and GLUCOSIDES.

MORITANNIC ACID *v.* OLD FUSTIC.

MORPHIGENINE. The hydrochloride of 9-amino-10-hydroxyphenanthrene.



MORPHINE *v.* OPIUM.

MORPHOSAN $C_{17}H_{19}O_3N(CH_3)Br,H_2O$ Trade name for a derivative of morphine. Used as a sedative and hypnotic. *v.* SYNTHETIC DRUGS.

MORTAR *v.* CEMENTS.

MORTAR, HYDRAULIC, *v.* CEMENTS.

MOSAIC GOLD. *Ormolu*, *v.* GOLD, MOSAIC.

MOSANDRITE. Hydrated titano-silicate of cerium earths (17–26·5 p.c.), calcium, &c., occurring as reddish-brown monoclinic crystals of prismatic habit in the nephelite-syenite of the Langesund-fjord in south Norway. Sp.gr. 2·93–3·03. The mineral is named after the Swedish chemist, C. G. Mosander (1797–1858), the discoverer of didymium, lanthanum, and terbium. L. J. S.

MOSLENE. A terpene $C_{10}H_{16}$, isolated as its nitrosochloride, white crystals, m.p. 111°, from the terpene fraction, b.p. 173°–175° (59°–60° /10 mm.) of the essential oil of *Mosla japonica* (Maxim), previously freed from *p*-cymene. Appears to be a dihydro-*p*-cymene (Y. Murayama Yakugakuzasshi, J. Pharm. Soc. Jap. 1921, 769). Found also in ajowan oil and the oil of *Mosla Grosseserrate* (Maxim).

MOSSITE *v.* TAPIOLITE.

MOTHER-LIQUOR. The liquid which remains after the crystallisation of a salt or other solid.

MOTHER-OF-PEARL. This is the nacreous lining of the shell of various molluscs, notably that of the large pearl-oyster *Meleagrina margaritifera* (Lam.). The nacre is secreted by the mantle of the mollusc, and consists mainly of calcium carbonate (the orthorhombic modification corresponding with the mineral aragonite) associated with organic matter (up to 12 p.c. of conchiolin). On digesting the nacre in a dilute acid, all the calcareous salt may be dissolved, leaving a coherent pellicle of connective tissue which retains the iridescence until disturbed by pressure. The iridescence is due to the interference of light reflected from the microscopi corrugated edges of the delicate layers of nacre. In consequence of its pleasing lustre, mother-of-pearl is largely employed for buttons, counters, card-cases, knife-handles, and a great variety of trivial ornaments. Large quantities are used by the manufacturers of Birmingham and Sheffield. An important use is that of inlaying papier-maché work, while it is also used in the ornamentation of Moorish and other Oriental furniture. Mother-of-pearl is sometimes decorated by engraving, especially by the Chinese, or by having a pattern etched upon it by means of acid. In trade three varieties of shell are recognised—namely, the white, the gold-edged, and the black-edged. Dark shells are known generally as 'smoked pearl.' The principal fisheries for pearl-shell are in Torres Straits, off the north-west coast of Western Australia, in the Sooloo Archipelago, in the Persian Gulf and Red Sea, and round Tahiti and some other islands of the South Pacific. The shell is commonly known in the market by the name of its place of shipment, such as 'Manila' and 'Egyptian' shells. In the Bay of California and the Gulf of Panama mother-of-pearl shell is obtained from the *Meleagrina californica* (Cpr.), and passes in trade as 'bullock shell.' The brilliant shells of the *Haliotis* and certain species of *Turbo* are also used for inlaid papier-maché and other ornamental purposes. *See* W. H. Dall, Amer. Nat. 1883, 27, 579; and E. W. Streeter, Pearls and Pearling Life, London, 1886; G. F. Kunz and G. H. Stevenson, The Book of the Pearl, New York, 1908. L. J. S.

MOTTRAMITE *v.* Vanadium, Psittacinite.

MOULDS, fermentations produced by, *v.* Fermentation.

MOUNTAIN ASH. *Sorbus Aucuparia* (Linn.) or [*Pyrus Aucuparia* (Gaert.)] *Service tree, Rowan.* The fruit of this plant affords one of the best natural sources of malic acid (*q.v.*) and of sorbitol. A partial analysis of the berries by Kelhofer (Chem. Zeit. 1895, 19, 1835) shows them to contain 2·78 p.c. free malic acid, 0·49 p.c. tannin, and 6·27 p.c. of sugar. Sorbinose is not present in the juice of the ripe berries, but on dilution and keeping for some months, is produced by the oxidation of the sorbitol (Freund, Monatsh. 1891, 11, 560). This oxidation is effected by a specific bacterium (Bertrand, Compt. rend. 1898, 127, 124, and 728). H. I.

MOUNTAIN BLUE. Syn. with *Azurite* $Cu(HO)_2 \cdot 2CuCO_3$, *v.* Copper.

MOUNTAIN CORK, FLAX, LEATHER, WOOD. See Asbestos.

MOUNTAIN GREEN. Syn. with *Malachite* (*q.v.*, also *v.* Copper). The term is also applied to a mixture of Schweinfurth green with gypsum or heavy spar; *v.* Arsenic.

MOUNTAIN SOAP. *Steatite v.* Talc.

MOWRAH SEED OIL *v.* Bassia oil.

MUCIC ACID *v.* Carbohydrates. Mucic acid is made commercially by an American company at Eureka, Montana, by Acree's process, which consists in treating larch sawdust with a hydrolytic agent, oxidising the resulting galactose with nitric acid, evaporating and crystallising. It is used as a substitute for cream of tartar in baking powder and is considered a safe food for diabetics.

MUCIC FERMENTATION GUM *v.* Gums.

MUCILAGE. The older writers made a distinction generally between gums which, like arabic and tragacanth, are obtained as a solid exudate, and the gum which is almost a universal constituent of plants, especially of some seeds and roots, and may be extracted by treatment with water (*cf.* Gm. 15, 209). The latter was termed *mucilage*, or *vegetable mucilage*, or *Pflanzenschleim* (Ger.). Among the more important sources of this gum are marshmallow, salep, fleawort, linseed, and quince; *v.* Gums.

MUCONIC ACID. $C_6H_6O_4$, or $CO_2H \cdot CH : CH \cdot CH : CH \cdot CO_2H$. A white crystalline solid, m.p. above 260°, formed by the action of alcoholic potash on $\beta\gamma$-di-bromo-adipic acid (Rupe, Annalen, 256, 22; Ruhemann and Blackman, Chem. Soc. Trans. 57, 373), slightly soluble in hot water, soluble in alcohol and acetic acid. Forms *i*-tartaric acid by oxidation with potassium permanganate, together with formic, carbonic, oxalic, mucic acids, &c. *Mucic acid* is obtained in yields up to 36 p.c. of the theoretical by oxidising a neutral solution of sodium muconate with sodium chlorate in presence of osmium tetroxide and a few drops of acetic acid (Behrend and Heyer, Annalen, 1919, 418, 294).

MUKOGEN *v.* Synthetic drugs.

MULBERRY, *Morus* spp. The name of several varieties of trees, grown for fruit, ornament, timber, shade, or for the sake of the leaves, which form the best food for silkworms. Many species and varieties are known, the three best known types being *M. alba* (Linn.), *M. nigra* (Linn.), and *M. rubra* (Linn.). Fresenius (Annalen, 185, 101, 219) found in the fruit of black mulberries—

Water	Protein	Free acid	Invert sugar	Pectins	Seeds and fibre	Ash
84·71	0·39	1·86	9·19	2·03	1·16	0·65

The leaves contain from 62 to 73 p.c. of water, and the dry matter contains from 3·8 to 6·1 p.c. of nitrogen and from 7 to 8·5 p.c. of ash (Sestini, Versuchs. Stat. Organ. 15, 286). Alpe (Bied. Zentr. 1900, 29, 422) estimates that in Italy about 20 kilos. of wood and 25 kilos. of leaves are removed from each tree annually, and that this robs the soil of about 510 grammes of N, 172 grammes of P_2O_5, and 486 grammes of CaO, a loss which could be made good by about 100 kilos. of farm-yard manure to each tree. Menozzi (Chem. Soc. Abstr. 1899, ii. 682) found the dry matter of mulberry leaves to contain 5·0 p.c. of pentosans and 11·2 p.c. of cellulose. For a detailed study of the nitrogenous compounds of mulberry leaves and particularly of the products of their hydrolysis *v.* Katayama (Bull. Imp. Sericult. Exper. Stat. Nakano, Tokyo, 1916, 1, 1; J. C. S. 1916, abst. i. 875). H. I.

MULBERRY PAPER. The inner bark of *Broussonetia papyrifera* (Vent.) contains bast-fibres which are used in China and Japan for the preparation of a kind of paper, and in Polynesia for the manufacture of a fabric.

MULHOUSE BLUE *v.* Triphenylmethane colouring matters.

MUM. A kind of fat ale, brewed from wheat and bitter herbs.

MUNDIC. The name given by the Cornish miners to iron pyrites. Similarly mispickel arsenical pyrites is known as 'arsenical mundic.'

MUNJEET or **MANJEET.** The *Rubia cordifolia* (Linn.) was formerly extensively cultivated in India, particularly in the mountainous districts, for the sake of the colouring matters contained in its stem or roots. In the Darjeeling district it occurs as a small climber common all over the hills, at elevations varying from 3000 to 7000 feet, but most abundant between 5000 and 6000 feet, and is found either creeping along the ground or climbing the trunks of trees in large festoons. In Bengal it would seem that the dye of munjeet is extracted mainly from the stem, and only occasionally from the root, as is the case in the North-Western Provinces and elsewhere in India. The munjeet of Bengal is apparently rather the *Rubia munjista* of Roxburgh than the *Rubia cordifolia*. This species of Roxburgh is, however, reduced to *Rubia cordifolia* in Hooker's Flora of British India. To prepare the dye the wood of the munjeet is first dried, then crushed and pounded, and then generally boiled with water, but sometimes merely left to steep in cold water. The solution obtained is of a deep red, and is used generally to dye coarse cotton fabrics, or the thread which is to be woven into such fabrics. Alum appears to be generally employed as a mordant, although myrobalans also are used in the Darjeeling district, and other astringents in the Maldah district. In the latter district munjeet is used in conjunction with iron salts to produce a deep purple, and in the Darjeeling district is mixed with indigo to form a maroon (McCann, Dyes and Tans of Bengal). The red and chocolates of East Indian chintzes were formerly entirely obtained from munjeet. The colours produced from munjeet are bright, but not so durable as those from ordinary madder, the inferiority being due, according to Stenhouse (Pharm. Jahr. 13, 148), to the presence of purpurin and an orange dye munjistin (purpuroxanthin carboxylic acid). Runge, who examined the tinctorial power of munjeet, concluded that it contained twice as much available colouring matter as madder, but later experiments have shown that the colouring power is actually less. Stenhouse found that munjeet garancine has only half the colouring power of garancine made from Naples roots, but that munjeet yields (according to Higgin) from 52–55 p.c. of garancine, whereas madder yields only 30–33 p.c.

When madder was so much in vogue, munjeet was employed to some extent in this country, because it was considered that a good quality of this material contained as much colouring matter as madder, and could be applied by exactly the same methods.

The important colouring matter of munjeet is *purpurin*, and no alizarin is present in this root, and it is therefore interesting to note that whereas chay root contains alizarin, and munjeet purpurin, in madder both these substances exist together.

For the analysis of the phenolic constituents of munjeet, a modification of the method of Stenhouse, who first submitted this plant to examination, is to be recommended.

The ground dyestuff is digested with boiling alum solution for 5 hours, and the deep red extract treated with acid and allowed to cool. The red precipitate is collected, washed and dried, and then extracted with boiling toluene (carbon disulphide was employed by Stenhouse), by which means the colouring matters pass into solution, and a resinous impurity remains undissolved. The colouring matters are now removed from the toluene by agitation with dilute potassium hydroxide solution, the alkaline liquid is acidified, and the precipitate collected, washed, and dried. In order to separate the constituents of this product it is extracted about ten times with boiling dilute acetic acid, and the dark red residue consisting of *purpurin* is crystallised from alcohol.

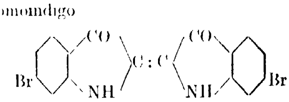
The earlier acetic acid extracts are mixed with hydrochloric acid, and the yellowish-red deposits are crystallised from alcohol. The product consists of orange-coloured leaflets, and is *purpuroxanthin carboxylic acid* or *munjistin*, as it was termed by Stenhouse, its discoverer, who first obtained it from munjeet. The properties of this compound have already been given in detail under MADDER.

Munjeet has also been examined by Perkin and Hummel, who, in addition to the above constituents, detected the presence of a trace of *purpuroxanthin* (Chem. Soc. Trans. 1893, 63, 115). A. G. P.

MUNTZ METAL *v.* ZINC.

MUREX *v.* PURPLE OF THE ANCIENTS.

The Tyrian or antique purple was mainly obtained from shell-fish, especially from *Murex brandaris*. Friedlander (Monatsh. 1907, 28, 991; 29, 247) has isolated 1·4 grams of a pure purple dye from 12,000 specimens of *Murex brandaris*, and has shown that it is identical with 6:6′-dibromoindigo



(Sachs and Kempf, Ber. 1903, 36, 3303) *v.* INDIGO, SYNTHETIC, and PUNICIN.

MUREXAN *v.* URAMIL.

MUREXIDE, *ammonium hydrogen purpurate* $C_8H_8O_6N_6,H_2O$. The formation of a red residue when a solution of uric acid in nitric acid is evaporated to dryness, was first observed by Scheele in 1776, and forms the basis of the well-known *murexide test* for uric acid and compounds related thereto. In 1818 Prout (Ann. Chim. 11, 48) obtained the coloured principle in a crystalline form, and regarded it as the ammonium salt of a hitherto unknown acid, which he named *purpuric acid*; and by double decomposition prepared several other red purpurates. Liebig and Wöhler (Annalen, 1838, 26, 319) showed that the compound obtained by the action of mineral acids on ammonium purpurate, and regarded by Prout as the free acid, was in reality 'murexan' (afterwards identified by Beilstein with *uramil*), which, together with alloxan, form the chief products of decomposition of purpuric acid by mineral acids. These authors therefore gave the name of *murexide* to the compound, regarding it as having more of the nature of an acid amide than of a true ammonium salt. Subsequent work has not justified this conclusion, however, since purpuric acid mixed with ammonium chloride can be obtained by the action of dry hydrogen chloride on murexide suspended in hot anhydrous acetic acid ; it is an orange-red powder, and forms soluble salts with organic bases such as methylamine, ethylamine, pyridine, quinoline, and aniline (Möhlau and Litter, J. pr. Chem. 1906, [ii.] 73, 449). *v.* Œschner de Coninck (Compt. rend. Soc. biol. 75, 558) for greater definition of the reaction.

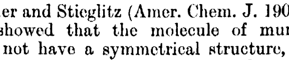
Preparation.—(1) From uric acid, by oxidising with nitric acid and subsequent treatment with ammonia or ammonium carbonate (Prout, *l.c.* ; Liebig and Wöhler, *l.c.* ; Kodweiss, Pogg. Ann. 19, 12 ; Fritzsche, Annalen, 1839, 32, 316).

(2) From alloxantin or alloxan by the action of ammonium salts in solution (Fritzsche, *l.c.* ; Liebig, *l.c.* ; Gregory, J. pr. Chem. [i.] 22, 374) ; or by passing dry ammonia over finely powdered alloxantin at 100° (Gmelin, Hand. f. Chem. 1856, iv. 195). According to Piloty and Finckh (Annalen, 1904, 333, 22), a yield of 80 p.c. of pure murexide can be obtained by adding 5 grams of alloxantin in 200 c.c. of water to a mixture of 25 grams of ammonium acetate in 100 c.c. water and 15 c.c. of 10 p.c. ammonia saturated with carbon dioxide ; the solutions are mixed at 80° and the murexide crystallises out. The alloxantin may be replaced by a mixture of ammonium dialurate and alloxan. Hartley (Chem. Soc. Trans. 1905, 1791) prepared spectroscopically pure murexide by passing a stream of dry ammonia into finely-powdered alloxantin mixed with 100 times its weight of boiling absolute alcohol, for 3 hours or more. The precipitated anhydrous murexide is washed with absolute alcohol and dried at 100°, or in a vacuum.

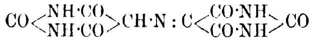
(3) From uramil by oxidation with mercuric oxide in the presence of ammonia (Liebig and Wöhler, *l.c.* ; Beilstein, Annalen, 1858, 107, 176) ; or by adding alloxan to a saturated solution of uramil in hot ammonia solution (Liebig).

The formation of murexide by the interaction of aqueous solutions of alloxan and amino acids was first observed by Strecker (Annalen, 1862, 123, 363). The reaction has been more closely investigated by Piloty and Finckh (*ibid.* 1904, 333, 22), and by Hurtley and Wootton (Chem. Soc. Trans. 1910, 99, 288). According to the latter authors, the amino acid is oxidised by the alloxan to the next lower aldehyde with the elimination of carbon dioxide and ammonia ; the alloxan is reduced to dialuric acid, which combines with the unchanged alloxan to form alloxantin, and this, with the ammonia, forms murexide. The red stain caused by alloxan on the skin is probably due to a similar reaction, and it is suggested that alloxan may prove a suitable reagent for the detection of amino acids

Constitution.—Matignon (Ann. Chim. Phys. 1893, [vi.] 28, 347) regarded purpuric acid as the imino derivative of alloxantin and expressed the constitution of its ammonium salt, murexide, by the formula

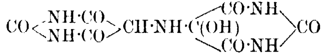


Slimmer and Stieglitz (Amer. Chem. J. 1904, 31, 661) showed that the molecule of murexide could not have a symmetrical structure, since the ammonium dimethylpurpurates obtained by the condensation of 1 : 3-dimethyluramil and alloxan, and of uramil and 1 : 3-dimethylalloxan are isomerides and not identical as would be the case if Matignon's formula were correct. These authors therefore suggest that the constitution of purpuric acid is best expressed by the formula



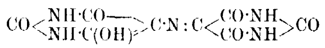
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH\cdot N : C}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

or in the hydrated form



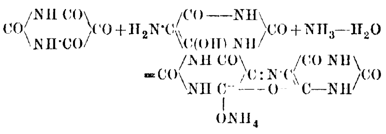
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH\cdot NH\cdot C(OH)}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

the salts being derived from the *pseudo* form of the acid

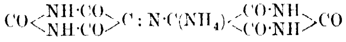


$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}—\\ \mathrm{NH\cdot C(OH)}\end{matrix}>\mathrm{C\cdot N : C}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

Piloty and Finckh (Annalen, 1904, 333, 22), having regard to the intense colour of murexide, assign to alloxan a quinonoid structure and to murexide that of a diurexide oxazonium ammonium salt, and express its formation from uramil, alloxan, and ammonia by the following scheme

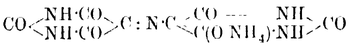


Möhlau and Litter (Ber. 1904, 37, 2686 ; J. pr. Chem. 1906, [ii.] 73, 449) represent murexide as a ketoimide having an unsymmetrical structure such as may be expressed by the formulæ



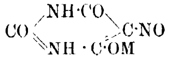
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{C : N\cdot C(NH_4)}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

or

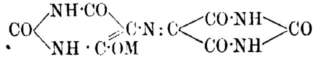


$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{C : N\cdot C}<\begin{matrix}\mathrm{CO\;—\;NH}\\ \mathrm{C(O\,NH_4)\cdot NH}\end{matrix}>\mathrm{CO}$$

The second of these is identical with that proposed by Slimmer and Stieglitz (*l.c.*) ; and deduced by Hartley (Chem. Soc. Trans. 1905, 87, 1794) from a study of the action of alcoholic ammonia on alloxantin. Hantzsch and Robison (Ber. 1910, 43, 92) point out the correspondence between their formula for the coloured salts of violuric acid and the above formula for murexide



Violurate.



Purpurate.

the oxygen of the nitroso group of the violurate, being replaced by a malonylurea residue.

Murexide crystallises in short four-sided garnet-red prisms, with gold-green reflex. The anhydrous salt forms a brownish powder which assumes a green metallic lustre when rubbed. Its molecular heat of combustion is 736·7 cal. (Matignon, Ann. Chim. 1893, [vi.] 28, 346), it is sparingly soluble in cold, more readily so in hot water, insoluble in alcohol or ether. The absorption spectrum shows two absorption bands, one in the visible spectrum and one in the ultra-violet (Hartley, Chem. Soc. Trans. 1887, 199 ; 1905, 1805).

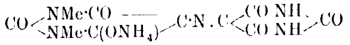
Solutions of murexide dye silk, wool, cotton, or leather red to purple shades in the presence of mercury salts, or orange to yellow shades in the presence of zinc salts, and at one time the compound was prepared on a commercial scale, as a dyestuff, from the uric acid extracted from guano. The fugitiveness of the colours in the presence of even sulphurous acid, and the superiority of the aniline dyes have caused it to be entirely superseded.

In addition to murexide, the following salts of purpuric acid have been described: *sodium hydrogen salt* $C_8H_4NaO_6N_5$, dark brick-red solid; *potassium hydrogen salt* $C_8H_4KO_6N_5$, dark red microcrystalline solid, prepared like the other salts from murexide by double decomposition, also by oxidising dipotassium uramil with iodine in ethereal solution (Piloty and Finckh, Annalen, 1904, 333, 22); di-*potassium salt* $C_8H_3K_2O_6N_5$, dark blue solid, formed by dissolving the mono-potassium salt in potassium hydroxide (Fritzsche); *calcium salt* $C_8H_3CaO_6N_5$, dark green crystalline precipitate (Beilstein); *barium salt* $Ba(C_8H_4O_6N_5)_2,3H_2O$, dark green precipitate, very sparingly soluble in water (Fritzsche); *silver salt* $C_8H_4AgO_6N_5,1\frac{1}{2}H_2O$, bright purple powder; a solution of murexide gives a red precipitate with lead acetate and a bronze red precipitate with mercuric chloride.

Methylamine purpurate $C_9H_{10}O_6N_6,H_2O$, prepared by the action of methylamine on alloxan and alloxantin, forms red microscopic rhombic crystals, loses H_2O at 110°, decomposes at 210°, and when heated with water yields 7-methyl uramil, alloxantin, alloxan, and methylamine.

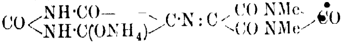
Ethylamine purpurate $C_{10}H_{12}O_6N_6,H_2O$ decomposes at 205° (Mohlau and Litter, J. pr Chem. 1906, [ii.] 73, 449).

Other derivatives of purpuric acid are: *ammonium*-1 : 3-*dimethylpurpurate*



$$CO\left\langle\begin{matrix}NMe\cdot CO-\!-\!-\!-\\NMe\cdot C(ONH_4)\end{matrix}\right\rangle C\cdot N.C\left\langle\begin{matrix}CO\,NH\\CO\,NH\end{matrix}\right\rangle CO$$

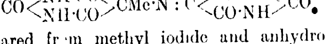
formed from 1 : 3-dimethyluramil and alloxan in the presence of ammonium carbonate, crystallises in small four-sided prisms, is slightly yellower in colour than murexide, and closely resembles its isomeride *ammonium* 1′ : 3′-*dimethylpurpurate*



$$CO\left\langle\begin{matrix}NH\cdot CO-\!-\!-\!-\\NH\cdot C(ONH_4)\end{matrix}\right\rangle C\cdot N:C\left\langle\begin{matrix}CO\,NMe\\CO\,NMe\end{matrix}\right\rangle CO$$

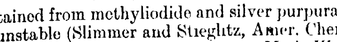
similarly obtained from uramil and 1 : 3-dimethyl alloxan.

5-*Methylpurpuric acid*



$$CO\left\langle\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}\right\rangle CMe\cdot N:C\left\langle\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\right\rangle CO,$$

prepared from methyl iodide and anhydrous potassium purpurate; the isomeric O-4-*methylpurpurate*



$$CO\left\langle\begin{matrix}NH-\!-\!-\!-CO\\NH\cdot C(OMe)\end{matrix}\right\rangle C\cdot N:C\left\langle\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\right\rangle CO$$

obtained from methyliodide and silver purpurate is unstable (Slimmer and Stieglitz, Amer. Chem. J. 1904, 31, 661). M. A. W.

MUREXOÏN (*tetramethylmurexide ?*)

$C_{12}H_{16}O_6N_6$

is prepared by the action of air and ammonia on dry or moist amalic acid (tetramethylalloxantin) (Rochleder, J. 1850, 436; Brunn, Ber. 1888, 21, 514); or by treating desoxyamalic acid with bromine, and afterwards with ammonia (Fischer and Ach, Ber. 1895, 28, 2477). It forms cinnabar-red four-sided prisms reflecting a golden yellow light from two faces, it sublimes at 230°, and decomposes without previous fusion at a higher temperature. It is sparingly soluble in alcohol or water, forming deep purple-red solutions. It is decomposed on warming with hydrochloric acid, but the only product of the reaction that has been identified is dimethylparabanic acid (cholestrophan) (Brunn, *l.c.*). M. A. W.

MURIATIC ACID *v.* Chlorine.

MUSCARINE, $C_5H_{15}O_3N$, an extremely toxic base, was first isolated from *Amanita muscaria* by Schmiedeberg and Koppe (*Das Muscarin*, Leipzig, 1869) and occurs in other poisonous fungi. Its constitution is unknown, but it was originally considered to be an oxidation product of choline Schmiedeberg and Harnack (Arch. exp Path. Pharm. 1877, 6, 101), by the action of nitric acid on choline, obtained a base which appeared to be identical with muscarine, and to have the constitution $OHN(CH_3)_3CH_2CH(OH)_2$. Muscarine was thus considered to be a hydrated aldehyde derived from choline. Differences in the physiological action of the synthetic and natural bases were, however, pointed out by Boehm (Arch. exp. Path Pharm. 1885, 19, 187), while the chemical constitution was placed in doubt by the work of Berlinerblau (Ber. 1884, 17, 1141), who synthesised the aldehyde corresponding to choline, and J E. Fischer (Ber. 1893, 26, 470), who confirmed the constitution of Berlinerblau's base by oxidation to betaine. The aldehyde differed considerably in its physiological action from both 'synthetic' and 'natural' muscarines. Nothnagel (Arch. Pharm. 1894, 232, 286) confirmed the earlier work from the chemical side, while Hans Meyer confirmed and extended Boehm's observations as to differences of physiological action.

The contradictory nature of these results was explained by the discovery (Ewins, Bio-Chem. J. 1914, 8, 209) that Schmiedeberg and Harnack's base was not an aldehyde but the choline ester of nitrous acid

$$OHN(CH_3)_3CH_2CH_2ONO$$

the nitrogen in the molecule, which here renders analysis difficult, not having been previously determined 'Synthetic' or 'pseudo' muscarine thus belongs to the series of choline esters, many of which, as shown by Hunt and Taveau (Hygien. Bull. No. 73, Washington, 1911), possess a very high degree of physiological activity. In particular another member of this series, acetyl-choline, which occurs in ergot (*q.v.*), has been shown by Dale (Jour. Physiol. 1914; Proc. Physiol. Soc. iii.) to approximate to the muscarine type of action.

Natural muscarine would not, however, appear to be an ester of choline, since its solutions are not decomposed by boiling dilute alkalis or acids. Investigation of a number of derivatives of choline (Ewins, Bio-Chem. J. 1914, 8, 366) revealed in some cases a very close resemblance in physiological action to that of muscarine, but the constitution of the latter remains unsolved. (*Cf.* Weinhagen, J. Amer. Chem. Soc. 1920, 42, 1670; Chem. Soc. Abstr. 1920, 118, i. 663.) G. B.

MUSCARINE, This name is also given to

$$\mathrm{ClN(CH_3)_2C_6H_3{<}\substack{N\\O}{>}C_{10}H_5OH}$$

the chloride of dimethyl phenyl-*p*-ammonium-*β*-hydroxynaphthoxazine, obtained by the action of nitrosodimethylaniline hydrochloride on *α*-dihydroxynaphthalene. A colouring matter introduced by Durand and Huguenin. Is a brownish-violet powder, sparingly soluble in cold water but readily soluble in hot water with a bluish-violet colour. Alkalis precipitate the base as a yellow-brown powder. Dyes cotton mordanted with tannin and tartar emetic a blue colour *v.* OXAZINE COLOURING MATTERS.

MUSCOVADA. The unrefined brown or raw sugar of commerce *v.* SUGAR.

MUSCOVITE or **MUSCOVY GLASS.** A term occasionally applied to mica (*q.v.*).

MUSHROOM, the name given to various species of edible fungi. Species of *Agaricus*, *Lactarius*, and *Coprinus*, and popularly even of *Boletus*, *Polyporus*, and *Morchella*, furnish most of the edible mushrooms, although some species of the same genera are poisonous. The following analyses, chiefly from Konig, are of edible fungi:—

	Water	Protein	Fat	Mannitol	Glucose	Other N-free extract	Crude fibre	Ash
Psalliota (*Agaricus*) *campestris* (Quel.)	89·7	4·9	0·2	0·4	0·7	2·5	0·8	0·8
Cantharellus cibarius (Fries.) . .	91·4	2·6	0·1	0·7	0·3	2·8	1·0	0·7
Boletus edulis (Bull.)	87·1	5·4	0·4	0·4	2·2	2·6	1·0	1·0
,, *luteus* (Linn.)	92·6	1·5	0·3	2·0		2·0	1·2	0·5
Lactarius deliciosus (Fries.). . . .	88·8	3·1	0·7	2·2		0·9	3·6	0·7
(?) *Polyporus ovinus* (Schäff.) . . .	91·6	1·0	0·6	2·6		1·7	1·8	0·7
Morchella esculenta (Pers.) . .	90·0	3·3	0·4	0·7	0·1	3·7	0·8	1·0
Coprinus comatus (Pers.)	94·3	2·0	0·1		2·9		0·2	0·5

Mushrooms are liable to considerable variation in composition according to the age at which they are gathered and to the character of the soil or other medium on which they are grown. The nitrogenous matter and crude fibre are the most variable constituents. Owing to the very large proportion of nitrogenous substances in the dry matter, mushrooms are usually considered to be highly nutritious, but, according to the investigations of Saltet (1885), Uffelmann, Strohmer (1886), and Mendel (1898), the nitrogenous matter has a low digestibility, about 33 p.c. of the pure proteids usually being indigestible. Of the total nitrogen, from 60–80 p.c. exists as proteid, 6-13 p.c. as amino acids, 11–17 p.c. as acid amides, and about 0·2 p.c. as ammonia. Choline occurs to the extent of 0·01 p.c. in *Cantharellus cibarius*, 0·015 p.c. in *Psalliota campestris*, and 0·0056 p.c. in *Boletus edulis* (Polstorff, Chem. Zentr. 1909, ii. 2014).

Lietz (Zeitsch. Nahrungm. Unters. Hygiene u. Waarenk. 1893, 7, 223) found that 19 varieties of mushrooms contained, in the dry matter, from 0·08 to 1·64 p.c. lecithin, and from 0·11 to 3·08 p.c. of combined phosphorus pentoxide.

Gilson (Compt. rend. 1895, 120, 1000) obtained, from various species, a substance identical with chitin, the horny external covering of insects. The fat consists of phytosterol and a dark brown oil, about half of which consists of free fatty acids, the remainder being neutral fat (Opitz, Arch. Pharm. 1895, 229, 290).

The non-nitrogenous extract of mushrooms consists chiefly of mannitol, trehalose (or mycose), inulin and pentosans. According to Bourquelot (Compt. rend. 108, 568) mannitol is largely produced from the trehalose during the after-ripening and drying, whilst the trehalose itself is formed from some dextrin-like carbohydrate, which constitutes the tissue of the fungus. The proportion of pentosans is small; Wittmann found about 0·1 p.c., whilst Menozzi (Chem. Soc. Abstr. 1899, ii. 683) found, in the dry matter of *Boletus edulis*, 1·9 p.c.

The ash varies in amount and composition; it forms from 5 to 9 p.c. of the dry matter, and usually contains about 50 p.c. K_2O, 30 p.c. P_2O_5, with smaller quantities of lime, magnesia, soda, silica, and chlorine. Alumina is often present, in some cases to the extent of 5–7 p.c. A poisonous fungus, *Amanita muscaria* (Pers.), contains an isomeride of betaine, *muscarine* $CH(OH)_2CH_2{\cdot}N(CH_3)_3OH$, which acts like a ptomaine. One of the edible fungi *Gyromitra* (*Helvella*) *esculenta* (Fries.) in the fresh state, contains a poisonous constituent, helvellic acid $C_{12}H_{20}O_7$ (Bohm and Kulz, Archiv. experimentelle Path. 19, 403). H. I.

MUSK. *Moschus.* U.S. P.; deleted from B. P. 1914. (*Musc*, Fr.; *Moschus*, Ger.). Musk consists of the dried secretion of the preputial follicles of the musk deer, *Moschus moschiferus* (Linn.), which inhabits the mountainous districts of Central Asia. *Cf.* Pereira (Mat. Med [iii.] 2, 2251). It is the most important article of export from Tibet, the principal market being at Tassienlou, in the principality of Kiala, which furnishes from 1200 to 1400 kilos. annually. Its value is now from 12 to 13 times its weight in silver. Three qualities are recognised by the Tibetans—first, golden-yellow; second, clear red-brown; and third, deep red-brown. It is largely adulterated by the addition of a mixture of blood, yolk of egg, and meat. An analysis by Geiger and Reimann, quoted by Gmelin (Handb. Chem. 2, 1449), shows that it contains cholesterol together with fatty, waxy, and albuminous substances. The well-known odour of musk is due to the presence of a ketone *muskone*. When distilled with steam crude musk yields 1·4 p.c. of a dark brown oil, about half of which distils at 200°–210° under 9 mm. pressure. Muskone $C_{15}H_{28}O$ or $C_{16}H_{30}O$ is obtained by treating the distillate with alcoholic potassium hydroxide and distilling the product at 160°–164° under 7 mm. pressure. It is a colourless, viscid oil, boils at 142°–143° under 2 mm., or with slight decomposition at 327°–330° under 752 mm. pressure. It is sparingly soluble in water, readily so in alcohol. The *oxime* melts at 46°. The *semicarbazone* melts at 133°–134°, and is odourless, but gives an odour of musk when heated with dilute sulphuric acid. The fraction of the oil boiling at 65°–106° under 7 mm. pressure obtained in the preparation of muskone has an unpleasant odour and gives the pine-wood reaction for pyrrole (Walbaum, J. pr. Chem. [ii.] 73, 488). Sack (Chem. Zeit. 1915, 39, 538) describes a different odorous ketone *civetone* (zebetone) $C_{17}H_{30}O$, m.p. 32°, b.p. 204°-205°/17 mm. or 342°/741·5 mm., giving an *oxime*, m.p. 92°, and a *semicarbazone*, m.p. 187°. Besides its use as a perfume, musk is employed in medicine as a nervous stimulant. According to Berthelot the odour of 10^{-17} gram may still be recognised. Bazzoni (J. Franklin Inst. 1915, 80, 463) found that the loss in weight of dry musk during 7 months in a current of dry air was about 7 p.c. of odorous constituents; when it ceased the musk was no longer odorous.

Compounds having the odour of musk have been prepared synthetically, but such substances have an entirely different chemical structure. These are, however, not poisonous, and are largely substituted in the cheaper forms of perfumery for the expensive natural product. The musk substitutes at present known are trinitro-*meta*-tertiarybutyltoluene and the corresponding compounds obtained from the homologues of toluene, and the dinitro derivatives of the ketones which are formed by the interaction of acyl chlorides on butyl derivatives of toluene and homologues (Baur, Compt. rend. 111, 238; Ber. 24, 2832; *ibid.* 31, 1344).

MUSK, ARTIFICIAL *v.* BUTYL.

MUSK-ROOT *v.* OLEO-RESINS.

MUSTARD. Mustard is derived from the seed of an annual cruciferous plant which grows wild or is cultivated in Great Britain, and throughout Europe, the United States, and many other countries. It grows to a height of from 3 to 6 feet, has yellow flowers and lyrate leaves.

Two varieties are commonly used, *Sinapis alba* (Linn.) or white mustard, and *Brassica nigra* (Koch) or black mustard. The seeds of the former are spherical, 2 to 3 mm. in diameter, of a buff colour outside, with a finely granular surface. Those of black mustard are from 1 to 1·5 mm. in diameter, have a dark brown reticulated surface, but are yellow within. Indian mustard is *Brassica juncea* (Coss.), and the Russian sarepta mustard is *B. Besseriana* (Andr.). The Dakota (wild) mustard or Charlock is *B. sinapistrum* (Boiss) (or *Sinapis arvensis* (Linn.)).

Preparation.—The ground farina is usually a mixture of the two varieties, and is prepared by crushing the seeds, winnowing out the husks, which form an obstacle to fine grinding, and sifting. A large proportion of the fixed oil is very generally removed by hydraulic pressure.

Composition.—The main constituent of the seed is the fixed oil, which is tasteless and nearly odourless, and is employed for mixing with other illuminating oils and sometimes for culinary purposes. This occurs in both varieties of the seed. The valuable and characteristic properties of mustard are due to the volatile oil, allyl *iso*-thiocyanate, C_3H_5NCS, which, however, is not present in the mustard as such, but is formed by the action of water and an enzyme, *myrosin*, which is present in both kinds of seed, on a glucoside, potassium myronate $KC_{10}H_{18}NS_2O_{10}$, which is only found in the black variety. White mustard also contains a glucoside, *sinalbin* ($C_{30}H_{42}N_2S_2O_{15}$), which on hydrolysis forms an acrid pungent oil, *acrinyl iso-thiocyanate* (C_7H_7ONCS), which, however, is only slightly volatile with steam. Mustard seeds contain mucilage but no starch.

Fairly complete analyses by Piesse and Stansell gave the following results—

TABLE I.

—	Whole seed		Farina	
	White	Brown	White	Brown
Moisture . .	8·66	8·52	6·04	4·83
Fat . . .	26·53	25·54	35·16	37·05
Cellulose . .	9·69	9·01	5·79	2·80
Sulphur . .	0·96	1·28	1·27	1·43
Nitrogen . .	4·51	4·38	4·73	4·75
Proteins . .	28·21	26·50	29·56	28·71
Myrosin & albumin	4·91	5·24	6·70	6·46
Soluble matter .	26·83	24·22	33·94	31·94
Volatile oil . .	0·07	0·47	0·03	1·44
Ash, total . .	4·63	4·98	4·28	4·93
Ash, soluble . .	0·65	1·11	0·44	0·92
Potassium myronate	—	1·69	—	5·15

Mustard is chiefly used as a condiment, but is also employed in medicine internally as an emetic and externally as a rubefacient and counter-irritant. The volatile oil, from black mustard seeds, is also official in the British Pharmacopœia, and is a powerful vesicant.

Table-mustard, as we use it to-day, is said to have been first prepared in 1720 by a Mrs. Clements, of Durham, who conceived the idea of grinding the seeds in a mill and mixing the powder with water. Before that time the seeds were sent whole to table.

Adulteration.—Practically the only adulteration to which mustard is subject in this country is the addition of foreign starches, accompanied not unfrequently by turmeric or aniline dyes to restore the colour. Cayenne pepper is also said to be added to increase the pungency.

The addition of starch is defended on the ground that it confers better keeping properties on the preparation and prevents it caking. Provided the addition is notified and the amount moderate there is no objection; but in England, at all events, it is quite unnecessary.

In inferior grades traces of starch may be present owing to the accidental admixture of starch-bearing seeds during the gathering of the crop.

The removal of the fixed oil has been regarded by some as an adulteration, and at least one successful prosecution has been recorded in this country (British Food Journal, 1903, 278). The practice, however, is very general, especially on the Continent, and little can be said against it. The fixed oil adds nothing to the flavour, and is certainly liable to become rancid.

The admixture of ground hulls in excessive proportion has also been recorded.

Detection of adulteration.—Added starch is detected by the microscope. If much is present the addition of iodine solution will stain the sample blue. As, however, the volatile oil absorbs iodine rapidly, it is desirable in the case of small quantities of starch, to prevent the formation of the volatile oil by previously boiling with potassium iodide (Amer. J. Pharm. 1898, 70, 433). The determination of the starch may be effected approximately by microscopical comparison of the sample with mixtures of mustard containing known weights of the particular starch ascertained to be present.

Methods based on the conversions of the starch into sugar and the estimation of the reducing power are not very satisfactory, owing to the presence of other reducing substances not derived from the starch. To obviate this as far as possible the conversion should be by diastase, and should be preceded by extraction with ether and 10 p.c. alcohol.

A method in which the starch is weighed as such is that of Kreis (Chem. Zeit. 1910, 1021), in which the substance is digested with alcoholic potash, the insoluble matter, after washing with alcohol, is heated with dilute sodium hydroxide, and the solution diluted and filtered and a portion of the filtrate treated with an equal volume of 95 p.c. alcohol. The precipitate is allowed to settle (aided by a centrifuge), filtered off, washed with 50 p.c., then with 95 p.c. alcohol, finally with ether and dried and weighed. An allowance of 3 p.c. should be made for non-starchy substances in the precipitate.

The proportion of added starch may also be calculated, in the absence of other adulterants, from the reduction in the percentage of nitrogen in the fat and water-free sample. Methods based on the determination of the fixed oil are obviously unreliable.

Turmeric is detected by the microscope or by soaking a strip of filter paper in an alcoholic extract of the sample, then in a solution of borax, and finally acidifying with dilute (2 p.c.) hydrochloric acid. When dry the paper will assume a rose-red colour, which turns deep blue with ammonia or olive-green with dilute caustic potash.

Aniline dyes may be detected by digesting the mustard with water containing a few drops of ammonia, filtering, acidulating with acetic acid and dyeing wool threads with the filtrate. According to Bohrisch (Zeit. f. Unter. Nahr. u. Genuss. 1904, (8), 286), the yellow colour produced by pure mustard is removed by washing with water, while that due to coal-tar dyes is not.

The presence of an undue proportion of the hulls is at once apparent on microscopic examination, the most characteristic structures being the cellular epidermal layer with its mucilage, the sub-epidermal cells with their thickened angles in the case of white mustard; also the palisade cells, yellow and not reticulate in white mustard, and brown and reticulated in the black variety. As will be seen from Table II. the indications of the microscope may be confirmed by chemical analysis, the total nitrogen, fibre, and copper reducing power, after treatment with diastase, being the most useful determinations

TABLE II.—ANALYSIS OF MUSTARD (Leach).

—	Flour					Hulls						Seeds				
	Black			White		Black		White				Black		White		
	English	Californian	German	German	Californian	English		English		Californian	German	Bari	Californian	English	Dutch	German
Moisture . .	5·55	7·23	9·50	7·47	5·09	6·83	8·67	6·46	5·36	9·12	8·46	5·88	6·49	6·43	5·93	6·69
Total ash . .	5·58	4·90	5·25	1·73	4·69	5·03	4·43	4·56	4·65	1·59	4·66	4·07	3·84	4·37	4·83	4·34
Water soluble ash	0·27	0·23	0·09	0·18	0·23	0·95	1·26	2·33	1·91	1·78	1·80	0·46	0·45	0·52	0·73	0·63
Ash insol. HCl .	0·08	0·13	0·50	0·35	0·29	0·14	0·23	0·05	0·22	0·05	0·04	0·22	0·21	0·16	0·33	0·56
Fat (ether extract)	17·46	20·64	16·28	12·65	25·95	13·81	10·51	7·03	6·63	7·79	6·17	37·81	35·39	27·45	30·84	27·19
Volatile oil .	3·98	4·67	3·09	0·00	0·00	2·26	1·83	0·00	0·00	0·00	0·00	2·76	2·91	0·00	0·00	0·00
Alcohol extract	25·31	19·22	21·98	24·21	20·78	14·21	14·15	11·07	10·46	8·51	8·07	13·70	14·26	16·31	14·98	17·75
Total nitrogen .	6·37	6·75	7·13	7·44	6·21	3·89	4·04	3·03	3·22	3·60	2·90	4·10	4·49	3·96	4·12	5·09
Crude fibre	3·28	2·27	2·45	1·87	2·21	10·90	11·34	16·46	17·69	16·08	18·95	4·41	4·21	4·95	6·53	4·87
Reducing matters (acid conversion)	11·89	4·87	5·63	6·12	5·75	9·90	14·05	20·40	20·00	19·90	17·35	7·34	6·94	8·42	10·06	9·35
Reducing matters (diastase method)	0·71	0·23	0·22	0·23	0·00	1·20	3·56	6·11	4·21	3·74	2·91	1·76	1·78	0·92	1·82	1·45

Cayenne pepper may be detected by the pungent taste of the residue obtained by evaporating the alcoholic extract on the water-bath, and the acrid fumes which it yields on gentle ignition.

The presence of other species of mustard which are more likely to occur in foreign brands is almost entirely a matter of microscopical examination (*v.* Winton, Microscopy of Vegetable Foods; also Pammel, Amer. Monthly Micr. Journal, 17, 206, and 213; Pharm. J. 1905, [74] 719).

Charlock, or wild mustard, may be detected by heating the mustard slightly with chloral hydrate, the reagent being made by dissolving 16 grammes of chloral hydrate in 10 c.c. of water to which 1 c.c. of hydrochloric acid has been added. Examined under a low power the palisade cells will have been stained a deep blood red.

As the efficiency of mustard for medicinal purposes depends on the proportion of volatile mustard oil, its determination is of some importance. Roeser's method (J. Pharm. Chim. 1902, 361) is carried out as follows: 5 grammes of the sample are mixed with 60 c.c. of water and 15 c.c. of 60 p.c. alcohol, allowed to stand for 2 hours and distilled into 10 c.c. of ammonia until two-thirds of the liquid has passed over; 10 c.c. of N/10 silver nitrate are added, and after standing for 24 hours the solution is diluted to 100 c.c. To 50 c.c. of the filtered solution are added 5 c.c. of N/10 potassium cyanide, and the excess of cyanide determined by titration with standard silver nitrate, using slightly ammoniacal 5 p.c. potassium iodide as indicator. The percentage of volatile oil is obtained by multiplying the number of c.c. of silver nitrate used up by the oil by 0·6274 (*v.* also German Pharmacopœia). (For proportion of volatile oil yielded by various kinds of mustard oil, *see* Ann. Falsi. 1909, 2, 215, and 12, 372.)

The following method (D. Raquet, Ann. Chim. anal. 1912, 17, 174), which is official in a modified form in the British Pharmacopœia, 1914, for the examination of the oil itself, may be employed. In a 250 c.c. flask mix 5 grammes of the mustard with 100 c.c. of water and 20 c.c. of 90 p.c. alcohol, close the flask and allow to stand for 6 hours, or heat to 35°C. for 1 hour. Distil 50 c.c. into a 100 c.c. flask containing 10 c.c. of ammonia, then add 20 c.c. of N/10 silver nitrate and continue the distillation until the liquid in the flask is nearly up to the mark, fit a long glass tube to the neck of the flask and heat to 85°C. for 1 hour. When cold dilute to 100 c.c., filter and titrate 50 c.c., after acidulating with nitric acid, with N/10 ammonium thiocyanate, using ferric ammonium sulphate as indicator.

The number of c.c. of silver nitrate used multiplied by 0·198 gives the weight of allyl iso-thiocyanate in 100 grammes of the mustard. Different kinds of black mustard yielded the following figures: English, 1·39; Greek, 1·20; French, 1·08; Sicilian, 0·99; Italian, 0·99; Bombay, 0·81.

Standards.—United States Dept. of Agriculture. Mustard seeds should be those of *S. alba*, *B. nigra*, and *B. juncea*. Ground mustard should consist of powdered mustard seeds with or without a portion of the hulls having been removed and from which a portion of the fixed oil has been expressed. Standard ground mustard is mustard yielding not more than 2·5 p.c. of starch by the diastase method and not more than 8 p.c. of ash. Leach (J. Amer. Chem. Soc. 1904, 26, 1210) suggests ash and starch as above, crude fibre not exceeding 5 p.c., nitrogen not less than 8 p.c. C. H. C.

MUSTARD GAS. *ββ′-Dichloroethylsulphide* $(CH_2Cl{\cdot}CH_2)_2S$. *See Ethylene thio-chlorides*, art. Ethyl.

MUSTARD OIL *v.* Oils, Essential.

MYCOSE, TREHALOSE. *v.* Carbohydrates.

MYDRIASINE. Trade name for atropine methyl bromide.

MYDROL. Trade name for iodomethylphenyl pyrazolone. A white, odourless powder, with a bitter taste, soluble in water (*v.* Synthetic drugs).

MYOCTONINE. *See* under Aconitine and the Aconite Alkaloids.

MYOKYNINE *v.* Betaines.

MYOSIN *v.* Proteins.

β-MYRCENE $C_{10}H_{16}$ or

$$CH_2 : CH{\cdot}C(CH_3) : CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3) : CH_2(?)$$

A colourless mobile hydrocarbon obtained by cautiously heating isoprene at 80°–90°: contains three double linkings, two of them in conjugated positions, b.p. 63°–63·5°/20 mm., 58°/13 mm. D_4^{20}0·8472 n_D^{26}1·53681. When heated at 60°–70° with barium peroxide and sodium, or sodium alone, or by standing at the ordinary temperature in contact with benzoyl peroxide, it is converted into 'normal' caoutchouc, whereas under similar conditions isoprene gives an 'abnormal' caoutchouc (Ostromisslenski and Koschelev, J. Russ. Phys. Chem. Soc. 1915, 47, 1928; Chem. Soc. Abstr. 1916, [i.] 274).

MYRICA NAGI (Thunb.). This is an evergreen tree belonging to the *Myricaceæ* met with in the sub-tropical Himalaya from the Ravi eastwards, also in the Khasia mountains, the Malay Islands, China, and Japan. It is the box-myrtle or *yangmæ* of China, and is synonymous with *M. sapida* (Wall.), *M. rubra* (Sieb. and Zucc.), and *M. integrifolia* (Roxb.). The bark is occasionally used as a tanning agent, and is said to have been exported from the North-West Provinces to other parts of India to the extent of about 50 tons per annum. In Bombay it is met with under the name of *kaiphal*, and in Japan as *shibuki*.

Myricetin $C_{15}H_{10}O_8,H_2O$, the colouring matter, can be isolated from an aqueous extract of the plant by a similar method to that which is serviceable for the preparation of fisetin (*see* Young Fustic) but is more readily obtained in quantity from the Japanese commercial 'shibuki' extract (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1287; and Perkin, *ibid.* 1902, 81, 204).

The extract is treated with ten times its weight of hot water to remove tannin, and when cold the clear liquid is decanted off, the residue washed twice in a similar manner, and well drained. The product is extracted with boiling alcohol, and the solution evaporated until crystals commence to separate. On cooling these are collected (the filtrate A being reserved), and washed first with strong and then with dilute alcohol. A complete purification is best effected by converting the colouring matter into its acetyl derivative, and when pure hydrolysing this in the usual manner. Myricetin crystallises in yellow needles, melting at about 357°, and closely resembles quercetin in appearance. Dilute potassium hydroxide solution dissolves myricetin with a green coloration, which, on standing in air, becomes first blue, then violet, and eventually brown coloured. Alcoholic lead acetate gives an orange-red precipitate, and ferric chloride a brown-black coloration.

With mineral acids in the presence of acetic acid the following compounds which crystallise in orange red needles have been prepared:

Myricetin sulphate $C_{15}H_{10}O_8{\cdot}H_2SO_4$, *myricetin hydrochloride* $C_{15}H_{10}O_8{\cdot}HCl$, *myricetin hydrobromide* $C_{15}H_{10}O_8{\cdot}HBr$, and *myricetin hydriodide* $C_{15}H_{10}O_8{\cdot}HI$. Alcoholic potassium acetate yields *monopotassium myricetin* $C_{15}H_9O_8K$. Bromination in the presence of alcohol gives *tetrabrom-myricetin ethyl ether* $C_{15}H_5O_8Br_4Et$, colourless needles, m.p. about 146° (Perkin and Phipps, *ibid.* 1904, 85, 62), and this is analogous to the behaviour of morin under similar circumstances. By the action of bromine in acetic acid *tetrabrom-myricetin* $C_{15}H_6O_8Br_4$, brown-red needles, m.p. 235°–240°, is produced.

When fused with alkali myricetin gives *phloroglucinol* and *gallic acid*. *Hexa-acetylmyricetin* $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, m.p. 211°–212°; *hexabenzoylmyricetin*

$$C_{15}H_4O_8(C_7H_5O)_6$$

colourless needles; *myricetin pentamethyl ether* $C_{15}H_5O_3(OCH_3)_5$, pale yellow needles, m.p. 138°–139°; *acetylmyricetin pentamethyl ether*

$C_{15}H_4O_3(OCH_3)_5C_2H_3O$, colourless needles, m.p. 167°–170°, have been prepared. *Myricetin hexamethyl ether* $C_{15}H_4O_2(OCH_3)_6$, colourless needles, m.p. 154°–156°; and *myricetin hexaethyl ether* $C_{15}H_4O_2(OC_2H_5)_6$, almost colourless needles, m.p. 149°–151°, may be obtained by means of methyl and ethyl iodides respectively. Myricetin-hexaethyl-ether platinichloride

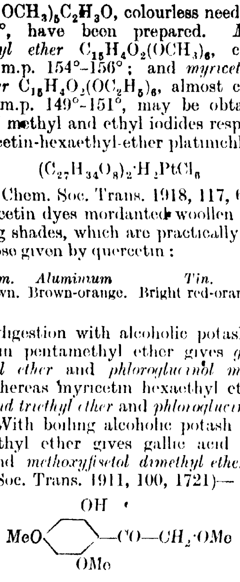
$$(C_{27}H_{34}O_8)_2 \cdot H_2PtCl_6$$

(Perkin, Chem. Soc. Trans. 1918, 117, 699).

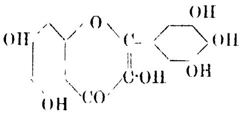
Myricetin dyes mordanted woollen cloth the following shades, which are practically identical with those given by quercetin:

Chromium.	*Aluminium*	*Tin.*	*Iron.*
Red-brown.	Brown-orange.	Bright red-orange.	Olive-black.

On digestion with alcoholic potash at 170° myricetin pentamethyl ether gives *gallic acid trimethyl ether* and *phloroglucinol monomethyl ether*, whereas myricetin hexaethyl ether gives *gallic acid triethyl ether* and *phloroglucinol diethyl ether*. With boiling alcoholic potash myricetin hexamethyl ether gives gallic acid trimethyl ether and *methoxyfisetol dimethyl ether* (Perkin, Chem. Soc. Trans. 1911, 100, 1721)—



Myricetin hexaethyl ether behaves similarly with production of gallic acid triethyl ether and *ethoxy fisetol diethyl ether*, prismatic needles, m.p. 96°–97°. Myricetin is therefore a *hydroxy quercetin*, and possesses the following constitution:



Myricitrin $C_{21}H_{22}O_{13},H_2O$, or rather

$$C_{21}H_{20}O_{12},2H_2O$$

the glucoside, is present in the alcoholic filtrate A, from the crude myricetin, from which it separates on standing. The crystals are collected, washed first with alcohol, then with dilute alcohol, crystallised from water, from alcohol, and finally from water. Myricitrin forms pale yellow, almost colourless leaflets, melting at 199°–200°, and is soluble in alkalis with a pale yellow tint. Aqueous lead acetate gives an orange-yellow precipitate, and alcoholic ferric chloride a deep greenish-black coloration. In appearance it cannot be distinguished from quercitrin, and the shades given by the two substances on mordanted woollen cloth are practically identical

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Full brown-yellow.	Full golden-yellow.	Lemon-yellow.	Brown-olive.

When hydrolysed with dilute sulphuric acid myricitrin yields rhamnose and myricetin, according to the equation—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_8+C_6H_{12}O_5$$

and is analogous to quercitrin which in a similar manner gives rhamnose and quercetin. In addition to myricetin the *M. nagi* contains a trace of glucoside of second colouring matter, which is probably *quercetin*.

The *dyeing properties* of myrica bark are generally similar to those of other yellow mordant dyestuffs. On wool with chromium mordant it gives a deep olive-yellow, and with aluminium a dull yellow, similar to the colours obtained from quercitron bark, but much fuller; with tin mordant it gives a bright red-orange, redder in hue than that given by quercitron bark; with iron mordant it gives a dark greenish-olive like that obtained from quercitron bark, but again fuller.

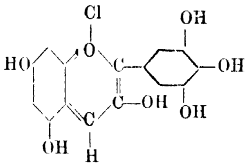
On cotton with aluminium and iron mordants it dyes colours which are more similar to those obtained from old fustic than from quercitron bark. Some specimens of myrica bark are exceedingly rich in colouring matter, and a sample examined by Hummel and Perkin (J. Soc. Chem. Ind. 1895, 14, 458) possessed much stronger dyeing power than old fustic.

According to Satow (J. Ind. Eng Chem. 1915, 7, 113) (Abst. Chem. Soc. 1911, 149), the colouring matter of the *M. rubra* has the formula $C_{15}H_{10}O_8$, and is identical in some of its properties with myricetin. By fusion with sodium polysulphide and sulphur a product is obtained which dyes cotton a deep sepia colour, though if copper sulphate, manganese sulphate, or ferrous sulphate is added to the fused mass, substances possessing a bluish or bluish-grey colour are produced. By fusing myricetin with sulphur alone a brown-yellow compound is obtained. A yellow dye may also be obtained by nitrating myricetin sulphonic acid

OTHER SOURCES OF MYRICETIN.

Sicilian sumach, the leaves of the *Rhus coriaria* (Linn.), contain myricetin, probably as glucoside (Perkin and Allen, *ibid.* 69, 1299). The colouring matter also exists in *Venetian sumach*, *R. cotinus*, and this is interesting, because the wood of this tree constitutes 'young fustic' and contains fisetin. Among other plants myricetin has been isolated from the *Myrica gale* (Linn.), the leaves of *Pistacia lentiscus* (Linn.), the leaves of the logwood tree, *Hæmatoxylon campechianum* (Linn.), and it is found in conjunction with quercetin in the leaves of the *coriaria myrtifolia* (Linn.) and the *R. metopium* (Linn.).

' Everest (Royal Soc. Proc. 1918, B., 90, 251) has shown that in all probability myricetin—as a glucoside—accompanies the anthocyanin pigment Violanin; a glucoside of



in the flowers of the purple-black viola (Sutton's 'Black Knight'), an observation which is of considerable interest in connection with the relationship which exists between the flavonols and anthocyans.

A. G. P.

MYRICA WAX (MEXICAN) v. WAXES.

MYRICIN. The portion of beeswax, consisting mainly of melissyl palmitate, left undissolved by boiling alcohol *v.* WAXES.

MYRICYL ALCOHOL $C_{31}H_{63}\cdot OH$ (Gascard, Compt. rend. 1920, 170, 886) *v.* WAXES.

MYRISTIC ACID, $C_{13}H_{27}\cdot COOH$, discovered by Playfair in nutmeg butter, from *Myristica moschata* (Annalen, 37, 155); is found also in otoba fat from *M. otoba* (Goirgey, *ibid.* 66, 314); in Dika bread (Oudemans, J. 1860, 322); in coco-nut oil; in butter; in the oil from quince seeds (Hermann, Arch. Pharm. 237, 367); and in wool fat (Darmstadter and Lifschütz, Ber 1896, 620; 1898, 97), and may be obtained by melting stearolic acid with potassium hydroxide. It crystallises in needles, m p 53·8°, b p. 121°-122° (0 mm) and 250·5° (100 mm.), sp.gr. 0·8622 at 53·8°/4°. It is insoluble in water, and only slightly volatile with steam.

Trimyristin or *trimyristil glyceride*

$$C_3H_5(C_{14}H_{27}O_2)_3$$

in which form myristic acid occurs in the various *Myristica* fats, crystallises from ether in needles, m.p. 55°. The barium salt is sparingly soluble in water and in alcohol.

MYRISTICA FATS comprise a number of fats *belonging to the family of Myristicaceæ. They are all characterised by a preponderant proportion of myristin and hence by high saponification values.* Some of these fats, like ochoco fat, consist almost entirely of myristin. The following fats—arranged, as far as is possible at present, in the order of the iodine values—include the better known members of this group: (*a*) nutmeg butter, mace butter; (*b*) Papua nutmeg butter; (c) fat from *Myristica malabarica*; (*d*) Kombo fat; (*e*) fat from *Myristica canarica*; (*f*) fat from *Myristica guatemalensis*, 13·8 p c.; (*g*) Ucuhuba fat, Bicuhyba fat; (*h*) Ochoco fat.

In addition to the foregoing members there must be also included in this group the fats from: (1) *Myristica otoba* (Humb. and Bonp.), which yields the commercial otoba fat or otoba wax; (2) *Virola sebifera* (Aubl.), a fat used in Guiana in the manufacture of soaps and candles; (3) *Myristica ocuba* (Humb. and Bonp.), known commercially as ocuba wax, used in Pará as a candle-making material; (4) *Virola Michelii* (Heckel), occurring in French Guiana; (5) *Staudtia kamerunensis* (Warb.).

(*a*) **Nutmeg butter**, mace butter, is obtained from the seeds of *Myristica officinalis* (Linn.) (*S. moschata* [Thunb.], *S. fragrans* [Houtt.]), a tree growing wild on the islands of the Indian Archipelago, notably Celebes, Sumatra, Java, Molucca, and the Banda Islands. The tree (or at least varieties thereof) is also cultivated in Ceylon, in the West Indies, Brazil, and Guiana The pericarp of the seed yields the arillus (mace) which is used in pharmacy, as a condiment for culinary purposes, and for the preparation of the ethereal oil contained in it. Formerly the small, as also the worm-eaten, rejected nuts which could not be exported were worked up for mace butter on the islands of the Indian Archipelago. The nuts were ground to a coarse meal, packed in sacks, and steamed for about 6 hours over boiling pots. The sacks were then placed in a strong press and subjected to pressure. The butter so obtained was a brownish mass. This was exported in the shape of bars (resembling soap bars) wrapped in coco-nut tree leaves (hence these bars were termed 'soap of Banda'). At present mace butter is chiefly obtained in European works (Holland, Germany) where the nuts are powdered and expressed when hot. The fat is also prepared in small quantities by extraction with petroleum spirit or ether, in pharmaceutical laboratories.

The world's annual production of nutmegs does not exceed 1500 tons. Only a small quantity is used in the manufacture of nutmeg butter, so that the price of the fat is somewhat high. The seeds contain 38-40 p.c. of fat. Nutmeg butter has the consistence of soft tallow, is of a yellowish colour, and has the strong taste and odour of nutmegs.

The commercial fat varies considerably in composition It contains from 4 to 10 p.c. of an essential oil (hence its saponification value does not exceed 190, and falls to as low a figure as 154) and contains chiefly trimyristin, in addition to a liquid fat and free fatty acids.

Cold alcohol dissolves the liquid fat, the free fatty acids, and the essential oil (unsaponifiable matter), leaving about 45 p c. undissolved. The undissolved portion yields, on crystallisation *from ether, pure trimyristin, melting at 55°.*

Boiling alcohol dissolves nutmeg butter almost completely. The solubility in alcohol is not only due to the high percentage of free fatty acids contained in commercial samples, but also to the ready solubility of myristin itself in alcohol.

A specimen of genuine mace butter obtained from Ceylon nutmegs by Power and Salway (Chem. Soc. Trans. 1907, 1653) had the following composition:

Essential oil	12·5	p.c.
Trimyristin	73·0	,,
Oleic acid, as glyceride . .	3·0	,,
Linolenic acid, as glyceride .	0·5	,,
Formic, acetic, and cerotic acids (very small amounts) . .	—	
Unsaponifiable matter . .	8·5	,,
Resinous material . . .	2·0	,,
	99·5	,,

The unsaponifiable matter consisted of a substance of the formula $C_{18}H_{22}O_5$ (amounting to about 5 p.c. of the expressed oil) and some myristicin $C_{11}H_{12}O_3$ and a very small amount of alcohol $C_{20}H_{34}O$, melting at 134°-135°. This alcohol is described as a 'phytosterol'; it differs from the ordinary phytosterol (sitosterol) in chemical composition, although it has the same melting-point.

Owing to the proportion of essential oil, which genuine mace butter contains, the refractive index is very high. Various specimens examined in the butyro-refractometer indicated from 77·5 to 85 scale divisions. The iodine value varied from 77 to 80, the Reichert-Meissl value was 4·1-4·2, and the melting-point only 25°-26°.

(*b*) **Papua nutmeg butter.** In consequence of the large demand for mace butter (nutmeg butter), this fat is frequently replaced by fats from other species of *Myristica*. Thus Papua nutmeg butter, the fat from *Myristica argentea* (Warb.), the so-called 'Papua nutmeg,' which grows wild in Dutch New Guinea, is substituted for genuine mace butter. Papua butter chiefly differs from genuine mace butter in containing no essential oil.

(*c*) **Fat from Myristica malabarica** (Lam.) is obtained from the seeds of *Myristica malabarica*, a tall evergreen tree growing in the forests of Konkan, Kanara, Malabar, and Travancore. The seeds contain 32 p.c. of shells, and yield about 40 p.c. of fat and resins. The mace from these seeds differs entirely from that of the genuine mace in containing no essential oil. These seeds, sold as 'Bombay seeds' ('Kaiphal') have been frequently confounded with the genuine seeds from *Myristica officinalis*. The fat from the kernels of 'Bombay seeds' differs entirely from the fat from *Myristica officinalis*, for its saponification value is about 190; it melts at 31°, has an iodine value of 50·4, and a Reichert-Meissl value of 1·1 only. In the butyro-refractometer it only indicates 48–49 scale divisions at 30°.

(*d*) **Kombo fat, kombo butter** is obtained from the seeds of *Myristica angolensis* (Welw.), *Pycnanthus Kombo* [Baillon] (Warb.). This tree is widely distributed in the Gaboon (known there as 'arbre à suif du Gabon,') in the Congo, Angola, and in Southern and Northern Nigeria. The fruit breaks up easily into two thick hard pieces of husk and an inner nut covered with a false arillus; hence the seeds which are frequently mistaken for nutmegs can be easily differentiated from official nutmegs. The saponification value of a specimen (examined in the Imperial Institute) was 183, the iodine value 33·7. The numbers refer to a fat refined from crude fat by treatment with alkali in order to remove the fatty acids. The original crude fat had iodine value 65·4, and saponification value 275, and contained about 14 p.c. of fatty acids.

(*e*) The seeds of **Myristica canarica** are derived from the 'candle nut tree,' growing in India on the Western Ghats, from the Konkan southwards. A sample of the entire seeds yielded 49·4 p.c. of fat; the mace, 54·6 p c. of fat; the kernels separated from the shells contained 64·76 p.c. of fat. The fat examined by D. Hooper (Agric. Ledger, 1907, No. 3) was light brown and crystalline, and gave, in the cold, with strong sulphuric acid a carmine-red colour. The saponification value was 215·02, the iodine value 26·64. The liberated fatty acids contained about 70 p.c. of myristic acid. Possibly identical with the fat last named is the fat from *Myristica surinamensis* (Roland) (*Virola surinamensis* [Warb.]), and perhaps also the fat from *Virola guatemalensis* (Warb.), obtained from 'wild nutmegs,' which do not contain an essential oil. These are occasionally imported into this country under the name 'oil nuts,' from Africa, as also from South America. The iodine value of a specimen of fat from *V. guatemalensis* ('African oil nut') examined by Grimme was 13·8, its saponification value 244, and the proportion of unsaponifiable matter 1·13 p.c.

(*g*) **Ucuhuba fat, Urucaba fat, Bicubyba fat** is obtained from the nuts of *Myristica* (*Virola*) *bicuhyba* (Humb.). It is stated that the fat from *Virola bicuhyba* is usually mixed in Brazil with that from *Myristica officinalis*, but genuine specimens submitted to the author do not bear this out. Owing to the crude method employed in its preparation, the fat brought into the market is yellowish-brown, and has an aromatic odour (due to a small quantity of an essential oil), recalling that of coco-nut oil. Ucuhuba fat consists of myristin and olein (about 20 p.c.), small quantities of an essential oil, of a resinous substance, and of a wax-like compound. The resinous substance is soluble in ether, hot alcohol, petroleum spirit, and chloroform. Genuine specimens examined in the author's laboratory melted from 35°–44·7°, had the saponification value 218·8, the iodine value 18·5, Reichert-Meissl value 2·68, lactones 3·15 p.c., unsaponifiable matter 3·05 p.c., and insoluble fatty acids 89·37 p.c.

(*h*) **Ochoco fat** is contained in the seeds of *Scyphocephalium ochocoa* (Warb.), a tree indigenous to the west coast of Africa. From a description published by Pierre it appears that the nuts have no arillus, and that they are non-dehiscent. The specimens examined by the author were identified by the Kew authorities as the kernels of *Scyphocephalium ochocoa*. The average weight of the kernels is 10 grams; the smallest weighing 5 grams, and the largest 12·5 grams. The kernels, together with the thin husks surrounding the endocarp, yield 58·8 p.c. of fat. By whatever process the fat is prepared, a dark brown colouring matter is at the same time extracted, which is tenaciously retained by the fat. This dark colouring matter is not only contained in the husks, but also in the membranous extension of the husk (spermoderm) which passes through the whole of the endosperm, in the form of irregular lamellæ radiating from the chalaza. As the examination of the dark fat offered some difficulties, the only way to obtain a fat free from colouring matter was to cut out the white endosperm carefully by hand. The amount of endosperm so obtained formed 84·7 p.c. of the kernels. These 84·7 p c. contained 69·4 p.c. of fat.

The white endosperm, on being extracted in the usual manner, yielded a perfectly white fat having saponification value 238·5, iodine value 1·72, and Reichert-Meissl value 0·65. The fat may therefore be considered as consisting of practically pure myristin, or at most of 98 p.c. of myristin and 2 p.c. of olein.

The natives apply the name 'ochoco' indiscriminately to several edible fruits, such as the fruits from *Lophira alata* (Banks.) ('niam fat'). J. L.

MYRISTICA SURINAMENSIS. The fruit of the *Myristica surinamensis* (Roland) was imported into Germany under the name of 'oil nut.' The nuts have the size and form of a cherry, with a dark-grey brittle shell inclosing a hard kernel. The kernels freed from shell, ground to powder, and extracted with ether, give 73 p.c. of fatty extract. The crude fat contains resin and a free acid. 100 parts of crude fat contain therefore 87 parts of pure substance. The pure fat has the formula $C_{45}H_{86}O_6$, which agrees with that of trimyristin. Like tristearin and tripalmitin, this body exists in different modifications with different melting-points. The trimyristin, saponified with alcoholic potassium hydroxide, yields myristic acid $C_{14}H_{28}O_2$. No other glycerides exist in this fat. The free acid in the crude fat was found to be myristic acid. Owing to the purity of the fat, and the absence of other glycerides, Reimer and Will recommend it as a source of pure myristic acid (J. Soc. Chem. Ind. 4, 746).

MYRISTICOL *v.* CAMPHORS.

MYROBALANS *v.* TANNINS.

MYRRH, MYRRHIN, MYRRHOL *v.* GUM RESINS.

MYRTILLIDIN, MYRTILLIN *v.* ANTHOCYANINS.

MYRTLE BERRY WAX *v.* WAXES.

MYRTLE OIL and MYRTOL (Umney, Imp. Inst. Jour. Scient. & Tech. Research Dept. 1896, 302; Schimmel, Chem. Zentr. 1910, i. 1719). This oil as used medicinally begins to boil at 160° and about 80 p.c. distils over up to 240°. The residue consists of high-boiling terpenes, partly resinised and partly polymerised. From the portion boiling between 160° and 240° by repeated fractional distillation the following constituents can be separated :—

A terpene $C_{10}H_{16}$ boiling between 158° and 160°, and having a specific rotation $[\alpha]_D = +36{\cdot}8°$. According to Bartolotti (Gazz. chim. ital. 21, 276) the b.p. is 154°–155°, $[\alpha]_D$ +59·3°. Its properties led Jahns to believe it to be right-handed pinene.

Cineol $C_{10}H_{18}O$, which, purified by Wallach's method, boiled constantly at 176°.

A camphor probably of the formula $C_{10}H_{16}O$, in small quantity, boiling at 195°–200°, $[\alpha]_D$ 24·8° (Bartolotti, *l.c.*). The therapeutic value of the myrtle oil is dependent on the amount of cineol present in it, the latter substance being identical with cajeputol and eucalyptol (E. Jahns, Arch. Pharm. 27, [iii.] 174; J. Soc. Chem. Ind. 8, 721).

According to Semmler and Bartelt (Ber. 1907, 40, 1363), myrtle oil contains in its high boiling fraction the ester of an alcohol $C_{10}H_{16}O$, which is called *myrtenol* and has b.p. 222°–224°/760 mm., sp. gr. 0·9763 at 20°, $[n]_D$ 1·49668 and $[\alpha]_D$ (in 100 mm. tube) +45° 45′ (according to Soden and Elze, b.p. 220°–221°, $[\alpha]_D$ 49° 25′). With phosphorus pentachloride it yields *myrtenyl chloride* $C_{10}H_{15}Cl$, b.p. 90°/12 mm., and on reduction with sodium, *d*-pinene is formed. On oxidation with chromic acid myrtenol yields an aldehyde *myrtenal* $C_{10}H_{14}O$, b.p. 87°–90°/10 mm., which yields an oxime, m.p. 71°–72°, and a nitrile, b.p. 100°–102°/10 mm. On hydrolysing the nitrile *myrtenic acid* $C_{10}H_{14}O_2$, b.p. 148°/9 mm., m.p. 45°, is produced. By reduction of the acid *dihydromyrtenic acid* $C_{10}H_{16}O_2$, b.p. 142°–144°/8 mm., is formed. When oxidised with alkaline permanganate myrtenol yields *d*-pinic acid $C_9H_{14}O_4$, b.p. 212°–216°/10 mm.

The characteristic odour of myrtle oil is due chiefly to the ester in the fraction of the oil boiling at 160°–180° (Soden and Elze, Chem. Zeit. 1905, 29, 1031; Bartolotti, *l.c.*).

Myrtle seed oil forms a yellow oil of characteristic flavour, is readily soluble in ether and turpentine, but less so in alcohol. It contains glycerides of oleic, linoleic, myristic, and palmitic acids (Scusti and Perciabosco, Gazz. chim. ital. 1907, 37, 483).

MYRTLE WAX (*Laurel wax, Bayberry tallow*) is obtained from the berries of various species of *Myrica*. In North America where the *Myrica* shrubs are common along the Atlantic sea-coast, the myrtle wax is obtained from *Myrica cerifera* (Linn.) and *Myrica carolinensis* (Willd.). In South America, notably in New Granada and Venezuela, it is obtained from *Myrica arguta* (Kunth), and *Myrica caracassana* (Humb., Bonpl. et K.), and in South Africa (Cape Colony) from *Myrica quercifolia* (Linn.), *Myrica cordifolia* (Linn.), *Myrica laciniata* (Willd.), and *Myrica serrata* (Lam.). In Abyssinia, myrtle wax is obtained from *M. ethiopica* (Linn.).

The myrica fruits are of the size of a pea, and are covered with a snow-white crust of fat, which is permeated with brown or black spots.

Myrtle wax is a glyceride and consists chiefly of palmitin with small quantities only of olein (Smith and Wade, Amer. Chem. J. 1903, 629). The iodine value of commercial samples varies between 2 and 4.

Myrtle wax worked up by itself does not yield useful candles; it can, however, be employed in the proportion of 20–25 p.c. as an addition to other candle material. In the United States 'beeswax' candles have been made which contain a notable amount of myrtle wax.

J. L.

MYTILITOL $C_6H_{12}O_5,2H_2O$. A cyclose occurring in the valve muscles of *Mytilus edulis*. Colourless, lustrous crystals, m.p. 259°; optically inactive; does not contain a methoxyl group. Forms a *penta-acetate*, microscopic needles, m.p. 157°–158°, and a *hexa-acetate*, m.p. 180°–181°. Mytilitol is probably methyl-*cyclo*-hexanehexol (Ackermann, Ber. 1921, 54, [B.] 1938; *cf.* Jansen (Zeitsch. physiol. Chem. 1913, 85, 231), who regards it as *cyclo*-hexanepentol and an isomeride of quercitol).

N.

NAGA RED. An azo dye derived from benzidene, used as a trypanocide in the treatment of nagana.

NAGYAGITE. A sulpho-telluride of gold and lead crystallised in the orthorhombic system. It contains Te 15·11–30·52, S 8·07–10·76, Sb 0–7·39, Pb 50·78–60·83, Au 5·84–12·75 p.c., with sometimes small amounts of silver, iron, and selenium. The formula is uncertain, and has been variously given as $(Pb,Au)_2(Te,Sb,S)_3$, $Au_2Pb_{14}Sb_3Te_7S_{17}$, and $AuPb_6Te_6S_8$. It forms tabular crystals and foliated masses of thin flexible lamellæ with a blackish lead-grey colour and bright metallic lustre. Hence the popular names 'black tellurium' and 'foliated tellurium' (Ger. *Blattertellur*). There is a perfect cleavage parallel to the surface of the plates. Sp.gr. 6·85–7·46; H. 1–1·5, being soft enough to make a lead-grey mark on paper. The mineral was formerly found in some abundance, with native gold, blende, and rhodonite, at Nagyag in Transylvania, and less commonly with antimonial ores at Offenbanya also in Transylvania. It has been reported from Colorado with other it as a source of pure myristic acid (J. Soc. Chem. Ind. 4, 746).

MYRISTICOL *v.* CAMPHORS.

MYROBALANS *v.* TANNINS.

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MYRTLE BERRY WAX *v.* WAXES.

MYRTLE OIL and **MYRTOL** (Umney, Imp. Inst. Jour. Scient. & Tech. Research Dept. 1896, 302; Schimmel, Chem. Zentr. 1910, i. 1719). This oil as used medicinally begins to boil at 160° and about 90 p.c. distils over up to 240°. The residue consists of high-boiling terpenes, partly resinised and partly polymerised. From the portion boiling between 160° and 240° by repeated fractional distillation the following constituents can be separated:—

A terpene $C_{10}H_{16}$ boiling between 158° and 160°, and having a specific rotation $[\alpha]_D = +36{\cdot}8°$. According to Bartolotti (Gazz. chim. ital. 21, 270) the b.p. is 154°–155°, $[\alpha]_D + 59{\cdot}3°$. Its properties led Jahns to believe it to be right-handed pinene.

Cineol $C_{10}H_{18}O$, which, purified by Wallach's method, boiled constantly at 176°.

A camphor probably of the formula $C_{10}H_{18}O$, in small quantity, boiling at 195°–200°, $[\alpha]_D$ 24·8° (Bartolotti, *l.c.*). The therapeutic value of the myrtle oil is dependent on the amount of cineol present in it, the latter substance being identical with cajeputol and eucalyptol (E. Jahns, Arch. Pharm. 27, [iii.] 174; J. Soc. Chem. Ind. 8, 721).

According to Semmler and Bartelt (Ber. 1907, 40, 1363), myrtle oil contains in its high boiling fraction the ester of an alcohol $C_{10}H_{16}O$, which is called *myrtenol* and has b.p. 222°–224°/760 mm., sp. gr. 0·9763 at 20°, $[n]_D$ 1·49668 and $[\alpha]_D$ (in 100 mm. tube) $+45°\ 45'$ (according to Soden and Elze, b.p. 220°–221°, $[\alpha]_D$ 49° 25′). With phosphorus pentachloride it yields *myrtenyl chloride* $C_{10}H_{15}Cl$, b.p. 90°/12 mm., and on reduction with sodium, *d-pinene* is formed. On oxidation with chromic acid myrtenol yields an aldehyde *myrtenal* $C_{10}H_{14}O$, b.p. 87°–90°/10 mm., which yields an oxime, m.p. 71°–72°, and a nitrile, b.p. 100°–102°/10 mm. On hydrolysing the nitrile *myrtenic acid* $C_{10}H_{14}O_2$, b.p. 148°/9 mm., m.p. 45°, is produced. By reduction of the acid *dihydromyrtenic acid* $C_{10}H_{16}O_2$, b.p. 142°–144°/8 mm., is formed. When oxidised with alkaline permanganate myrtenol yields *d*-pinic acid $C_9H_{14}O_4$, b.p. 212°–216°/10 mm.

The characteristic odour of myrtle oil is due chiefly to the ester in the fraction of the oil boiling at 160°–180° (Soden and Elze, Chem. Zeit. 1905, 29, 1031; Bartolotti, *l.c.*).

Myrtle seed oil forms a yellow oil of characteristic flavour, is readily soluble in ether and turpentine, but less so in alcohol. It contains glycerides of oleic, linoleic, myristic, and palmitic acids (Scusti and Perciabosco, Gazz. chim. ital. 1907, 37, 483).

MYRTLE WAX (*Laurel wax, Bayberry tallow*) is obtained from the berries of various species of *Myrica*. In North America where the *Myrica* shrubs are common along the Atlantic sea-coast, the myrtle wax is obtained from *Myrica cerifera* (Linn.) and *Myrica carolinensis* (Willd.). In South America, notably in New Granada and Venezuela, it is obtained from *Myrica arguta* (Kunth), and *Myrica caracassana* (Humb., Bonpl. et K.), and in South Africa (Cape Colony) from *Myrica quercifolia* (Linn.), *Myrica cordifolia* (Linn.), *Myrica laciniata* (Willd.), and *Myrica serrata* (Lam.). In Abyssinia, myrtle wax is obtained from *M. æthiopica* (Linn.).

The myrica fruits are of the size of a pea, and are covered with a snow-white crust of fat, which is permeated with brown or black spots.

Myrtle wax is a glyceride and consists chiefly of palmitin with small quantities only of olein (Smith and Wade, Amer. Chem. J. 1903, 629). The iodine value of commercial samples varies between 2 and 4.

Myrtle wax worked up by itself does not yield useful candles; it can, however, be employed in the proportion of 20–25 p.c. as an addition to other candle material. In the United States 'beeswax' candles have been made which contain a notable amount of myrtle wax.

J. L.

MYTILITOL $C_7H_{14}O_6,2H_2O$. A cyclose occurring in the valve muscles of *Mytilus edulis*. Colourless, lustrous crystals, m.p. 259°; optically inactive; does not contain a methoxyl group. Forms a *penta-acetate*, microscopic needles, m.p. 157°–158°, and a *hexa-acetate*, m.p. 180°–181°. Mytilitol is probably methyl-*cyclo*-hexanehexol (Ackermann, Ber. 1921, 54, [B.] 1938; *cf.* Jansen (Zeitsch. physiol. Chem. 1913, 85, 231), who regards it as *cyclo*-hexanepentol and an isomeride of quercitol).

N.

NAGA RED. An azo dye derived from benzidene, used as a trypanocide in the treatment of nagana.

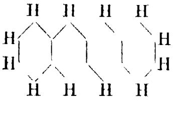
NAGYAGITE. A sulpho-telluride of gold and lead crystallised in the orthorhombic system. It contains Te 15·11-30·52, S 8·07–10·76, Sb 0–7·39, Pb 50·78–60·83, Au 5·84–12·75 p.c., with sometimes small amounts of silver, iron, and selenium. The formula is uncertain, and has been variously given as $(Pb,Au)_2(Te,Sb,S)_3$, $Au_2Pb_{14}Sb_3Te_7S_{17}$, and $AuPb_6Te_4S_6$. It forms tabular crystals and foliated masses of thin flexible lamellæ with a blackish lead-grey colour and bright metallic lustre. Hence the popular names 'black tellurium' and 'foliated tellurium' (Ger. *Blättertellur*). There is a perfect cleavage parallel to the surface of the plates. Sp.gr. 6·85–7·46; H. 1–1·5, being soft enough to make a lead-grey mark on paper. The mineral was formerly found in some abundance, with native gold, blende, and rhodonite, at Nagyag in Transylvania, and less commonly with antimonial ores at Offenbanya also in Transylvania. It has been reported from Colorado with other gold tellurides, and from Tararu Creek in New Zealand. L. J. S.

NAPELLINE. A name applied by Hubschmann to what was probably a mixture of amorphous alkaloids from *Aconitum Napellus* (Linn.). *See* ACONITE AND THE ACONITE ALKALOIDS.

NAPHTHA. This term was originally applied to a number of volatile, more or less mobile, inflammable liquids, usually ethers obtained by distillation, *e.g.* *Naphtha vitrioli* (ethyl ether), *N. nitri* (nitrous ether), *N. aceti* (acetic ether). The term was subsequently restricted to the naturally occurring liquid hydrocarbons, but was afterwards extended to other hydrocarbons obtained by the destructive distillation of shale, coal, bone, &c.

An artificial naphtha of a composition similar to the natural variety may be obtained, in small quantity, by passing a mixture of hydrogen and acetylene over nickel at 300° (Charitschkoff, J. Russ. Phys. Chem. 1906, 38, 878). The chemical characters of the naturally occurring naphthas differ widely, especially in the amount of the aromatic hydrocarbons they contain and in the nature of their paraffins and olefines. They are also characterised by variations in their optical properties. The origin of naturally occurring naphthas has given rise to much discussion, but all the available geological data testify that original deposits of naphtha occur only where there has been life. Support to the theory of organic origin is also given by the investigations of geologists and biologists on the destruction of life on the shores of seas and oceans such as is occurring at the present time in the Black Sea (Ipatieff, J. Russ. Phys. Chem. Soc. 1911, 43, 1437). According to Charitschkoff the natural naphthas are derived from the decomposition of asphalt, itself formed by the polymerisation of unsaturated hydrocarbons formed from carbides as surmised by Mendeléeff, Berthelot, and Cloez. The decomposition products of distilled Russian asphalt are similar to many Russian mineral oils (Charitschkoff).

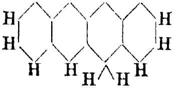
NAPHTHACENE



is obtained by the distillation of dihydroxynaphthacene quinone (isoethine diphthalide) with zinc-dust (Gabriel and Leupold, Ber. 1898, 31, 1272; Fr. Pat. 320327, 1902; J. Soc. Chem. Ind. 1903, 22).

It forms orange-yellow to red-yellow leaflets, m.p. about 335°, which sublime forming a greenish-yellow vapour. It gives a green solution with sulphuric acid, and is insoluble in benzene. When treated with fuming nitric acid it yields naphthacenequinone.

Dihydronaphthacene



is formed by the distillation of naphthacene or of dihydroxynaphthacene quinone over zinc-dust; or by heating dihydroxy- or dichloronaphthacene quinone with hydrogen iodide and phosphorus (Gabriel and Leupold, *l.c.*). It forms flat needles, m.p. 206° 207°, b.p. about 400°. It gives a green solution in sulphuric acid with evolution of sulphur dioxide; is sparingly soluble in boiling alcohol, but more readily so in benzene, glacial acetic acid, and other organic solvents. It is oxidised by chromic acid, forming naphthacenequinone, whilst with concentrated nitric acid it yields a nitronaphthacenequinone.

NAPHTHACENEQUINONE *v.* QUINONES.

NAPHTHALENE $C_{10}H_8$.[1]

History.—The production of naphthalene in the manufacture of coal-gas seems to have been noticed first by Clegg (*cf.* Brande, Quart. Journ. Sci. 1820, 8, 287); the discovery of its presence in coal-tar, however, was made simultaneously in 1819 by Garden (Annals Phil. 1820, 15, 74) and Brande (*l.c.*), the latter regarding it as a hydrocarbon (*cf.* Thomson, Schweig. J. 47, 337). It was further examined by Kidd, who named it 'naphthaline' (Phil. Trans. 1821, 209), by Ure (Phil. Trans. 1822, 473), and by Chamberlain (Annals Phil. 1823, [ii.] 6, 135); but its composition was determined first by Faraday in the course of his investigation of its isomeric monosulphonic acids (Phil. Trans. 1826, 159) and later by Laurent (Annalen, 1832, 3, 11). A bibliography of the early history of the subject is given in Gmelin (Eng. ed. 14, 1).

Formation and sources.—Naphthalene is almost invariably a constituent of the products obtained when organic substances are heated at a comparatively high temperature. For example, it is formed in small quantity, with other aromatic hydrocarbons, when marsh gas or acetylene (Berthelot, Bull. Soc. chim. 1867, [ii.] 7, 306), or the vapour of alcohol acetic acid (Berthelot, Ann. Chim. Phys. 1851, [iii.] 33, 295), toluene, xylene, or cumene, or of a mixture of benzene, styrene or anthracene with ethylene (Berthelot, Compt. rend. 1866, 63, 790, 834;

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[1] The following abbreviations are employed for the names of firms to which frequent reference is made in the text of this article:—

Aktienges.	Aktiengesellschaft fur Anilinfabrikation in Berlin
Badische	Badische Anilin- und Soda-Fabrik in Ludwigshafen a. Rh.
Bayer	Farbenfabriken vorm. F. Bayer & Co. in Elberfeld.
Bindsch.	Basler chemischer Fabrik, vorm. Basler chem. Fabrik Bindschedler in Basel.
Bronner	Farbfabrik vorm. Bronner in Frankfurt a. M.
Cassella	Anilinfarbenfabrik von L. Cassella & Co. in Frankfurt a. M.
Dahl	Dahl & Co. in Barmen.
Geigy	Anilinfarben- und Extrakt-Fabriken vorm. J. R. Geigy in Basel
Gesellsch.	Gesellschaft fur chemische Industrie in Basel
Griesheim	Chemische Fabrik Griesheim-Elektron in Frankfurt a. M.
Heyden	Chemische Fabrik von Heyden, Aktiengesellschaft in Radebeul bei Dresden.
Hochst	Farbwerke vorm. Meister, Lucius & Brüning in Hochst a. M.
Kalle	Kalle & Co., Aktiongesellschaft in Biebrich a. Rh.
Landshoff	Chemische Fabrik Grünau, Landshoff und Meyer
Leonhardt	Farbwerk Mülheim vorm. A. Leonhardt & Co. in Mülheim bei Frankfurt.
Sandoz	Chemische Fabrik vorm. Sandoz in Basel.
Schollkopf	Schöllkopf Aniline and Chemical Co., Buffalo (U.S.A.).
Verein	Verein chemischer Fabriken in Mannheim.

Bull. Soc. chim. 1866, [ii.] 6, 268; 1867, [ii.] 7, 218, 278, 285), is passed through a porcelain tube filled with pumice and heated to redness. It is present in small quantity in oil gas tar (Armstrong and Miller, Chem. Soc. Trans. 1886, 49, 80), and is produced when the vapour of toluene, or ethylbenzene, or of a mixture of toluene and ethylene is passed through a red-hot tube (Ferko, Ber. 1887, 20, 660) Berthelot's results have not been confirmed in every instance by later investigators (*cf.* Graebe, Ber. 1874, 7, 49; Lorenz, *ibid.* 1097; Carnelley, Chem. Soc. Trans. 1880, 37, 705; Ferko, *l.c.*), but this lack of confirmation may have been due to a difference in the conditions employed. Naphthalene is a constituent of brown coal-tar (Heusler, Ber. 1897, 30, 2744); also of the tar produced when turpentine vapour is led through a red-hot iron tube (Schultz, Ber. 1877, 10, 116), and is formed when colophony or gum benzoin is distilled with zinc-dust (Ciamician, Ber. 1878, 11, 269).

With the object, primarily, of obtaining benzene, toluene, and anthracene, petroleum residues and the high-boiling oils of wood tar and brown coal tar have been passed, as in Berthelot's experiments, through red-hot tubes filled with charcoal, pumice, &c. The tars formed under these conditions from the residues of Baku petroleum (Letny, Ber. 1878, 11, 1210, Dingl. poly. J. 1878, 229, 355; Lissenko, Ber. 1878, 11, 342; Rudnew, Dingl. poly. J. 1881, 239, 72), and from the high-boiling oils of brown coal tar (Liebermann and Burg, Ber. 1878, 11, 723; Salzmann and Wichelhaus, *ibid.* 1431), and pinewood tar (Atterberg, *ibid.* 1222) contain considerable quantities of naphthalene, and in general resemble coal tar. From a study of the equilibria among aromatic hydrocarbons produced by 'cracking' petroleum, the conclusion has been drawn that naphthalene begins to be formed at about the point where the toluene-xylene content passes its maximum (Rittmann and Twomey, J. Ind. Eng. Chem. 1916, 8, 20), the temperature at which it made its appearance being 750° in the case of a 'gas oil' obtained in refining crude Pennsylvanian petroleum (Egloff and Twomey, J. Physical Chem. 1916, 20, 145).

Naphthalene is a constituent of the principal varieties of tar produced from coal in the manufacture of gas and coke under ordinary conditions, but not of low temperature tar. By thermal decomposition of a tar obtained by distillation of coal *in vacuô* at 450°, it has been shown that at 750° the higher olefines, which are at a maximum at 550°, virtually disappear, and that their disappearance synchronises with the appearance of naphthalene in the distillate (Jones, J. Soc. Chem Ind. 1917, 36, 5). Naphthalene is also present in coal gas, although the amount is kept as small as possible, to avoid blocking of the service pipes during cold weather (*cf.* Smith, J Soc. Chem. Ind., 1889, 8, 949; Young, *ibid.* 1899, 18, 1109; 1900, 19, 813; Irwin, *ibid.* 314; also, art. GAS, COAL). The proportion in gas tar varies considerably with the different kinds of coal employed (*cf.* Smith, J. Soc. Chem. Ind 1889, 8, 951), and is greater the higher the temperature used during carbonisation (Smith, *ibid.* 1884, 3, 64), amounting usually to 4–6 p.c. (*ibid.* 1890, 9, 446), but in some cases to as much as 10 p.c. (Lewis, J. Gas Lighting, 1886, 47, 1248). In coke-oven tars, the proportion of naphthalene, as of other aromatic hydrocarbons, depends on the type of oven used (*cf.* Smith, J. Soc. Chem. Ind. 1883, 2, 401). With closed ovens, the tars do not differ greatly from gas tar, thus Watson Smith found from 1 to 10·17 p.c. in tars from Simon-Carvès ovens working with different kinds of coal (J. Soc. Chem. Ind. 1883, 2, 500; 1884, 3, 104, 508; J. Iron and Steel Inst 1885, 103), and 'an equal amount to that contained in gas tar' in the tar from an Otto oven (J. Soc. Chem. Ind. 1884, 3, 508; *cf.* Knublauch, Dingl. poly. J. 1884, 254, 37; Lunge, J. Soc. Chem. Ind. 1887, 6, 583). Blast-furnace tar contains only a very small proportion of naphthalene (Smith, J Soc. Chem. Ind. 1883, 2, 495).

Synthetical methods of preparing naphthalene have been described by Aronheim (Ber. 1873, 6, 67), Wreden and Znatowicz (Ber. 1876, 9, 1606), and Baeyer and Perkin (Ber. 1884, 17, 448). According to Bradley and Jacobs, it can be obtained by heating barium carbide with barium hydroxide at 800°–1000° (D. R.-P. 125936; Eng. P. 26061 of 1898).

Isolation and purification (Lunge, Coal Tar and Ammonia, 5th ed. 1916, 825 *et seq.*).—Naphthalene occurs in the coal tar fraction boiling at 180°–250°, and is present, therefore, in the 'light oil' (b.p. 110°–210°), and 'creosote oil' (b.p. 240°–270°), but most abundantly in the 'carbolic oil' (b.p. 210°–240°) of the tar distiller. From the carbolic oil the crude hydrocarbon crystallises out to a large extent on cooling, and can be freed from the accompanying oil by draining and subsequent hot-pressing. It is then stirred for some time with hot caustic soda solution of convenient strength to remove phenolic constituents; and, after the alkaline liquor has been run off, is washed with hot water. Next, it is heated for about an hour with 5–10 p.c. of concentrated sulphuric acid (sp gr. 1·7–1·81) [1] at about 100°, to remove both basic substances and residual phenols as soluble sulphonic acids. It is then washed several times with hot water, afterwards with weak alkali, and again with hot water, and finally is either sublimed or preferably distilled, pure naphthalene being collected between 210° and 230°, or so long as a sample solidifies on cooling, and gives only a faintly-coloured solution when dissolved in hot sulphuric acid.

The use of sulphuric acid may be avoided by blowing air, as finely divided as possible, into crude naphthalene heated at 200° during 10 hours. From 10 to 15 p.c. of the melt volatilises and, condensed, can be added to the next batch. The impurities, resinified and rendered non-volatile, remain behind when the purified naphthalene is separated by distillation and may be used as fuel (Ges. fur Teerverwert. D. R.-P. 277110).

Properties.—Purified naphthalene is usually found in commerce in white crystalline masses or thin scales. It crystallises from alcohol in scales or monoclinic prisms (Groth, Ber. 1870, 3, 453), melts at 80°, solidifies at 79·6°–79·8°

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[1] To obtain naphthalene which will remain permanently white an oxidising agent—for example, about 5 p.c. of finely ground pyrolusite, or Weldon-mud—may be used with the acid (Lunge, Ber. 1881, 14. 1756).

(Weger, Z. angew. Chem. 1909, 22, 341), and boils at 217·5° at 750·5 mm., or 218·5° at 767·6 mm. (Crafts, Bull. Soc. chim. 1883, [ii.] 39, 282) Its sp.gr. is 1·1517 at 18·75° (Vohl, J. pr. Chem. 1867, 102, 30), or 0·9774 in the liquid state at 79·2° (Kopp, Annalen, 1855, 95, 335; *cf.* Schiff, *ibid.* 1884, 223, 261). Naphthalene has a characteristic, penetrating, tarry odour, a pungent taste, and burns with a very smoky flame. It is only sparingly soluble in light petroleum, but very soluble in benzene or ether, and miscible in all proportions with hot toluene or absolute alcohol. Bechi found that 100 parts of toluene dissolve 31·94 parts of naphthalene at 16·5°, and 100 parts of absolute alcohol dissolve 5·29 parts at 15° (Ber. 1879, 12, 1978), and Smith that 100 parts of benzene, toluene, 'xylene,' and 'cumene' dissolve 45·8, 32·0, 31·5, and 30·1 parts of naphthalene respectively at 15° (J. Soc. Chem. Ind. 1902, 21, 1225). In tetralin, it dissolves in all proportions at 30°, but the solubility falls to 1 in 10 at 10° and at 6° is negligible (Kutschenreuter, D. R.-P. 317364). Naphthalene volatilises at temperatures considerably below its boiling-point, and is readily volatile with steam, alcohol vapour, or the vapour of tars of low boiling-point. According to Naumann (Ber. 1877, 10, 2016; 1878, 11, 33), when steam is passed into it, naphthalene distils with water in the following ratios.—

Barometer (cor.)	Temperature of liquid	Temperature of vapour	Ratio of naphthalene to water in distillate
mm			
759·5	97·8°	99·2°	100 : 520
757·0	97·7°	99·1°	100 : 570
733·0	—	98·2°	100 : 555

His values for the vapour pressure of naphthalene, *viz.* 2 mm. at 15°, 9 mm. at 78°, and 20·5 mm. at 100°, are higher than those of Barker—0·064 mm. at 20°, 7·4 mm. at 80°, and 18·5 mm. at 100° (Z. physikal. Chem. 1910, 71, 235).

Reactions.—Pure naphthalene in acetic acid solution is readily hydrogenated at 20° in the presence of platinum black,[1] yielding the *decahydride* (Willstatter and Hatt, Ber. 1912, 45, 1474). Hydrogenated, with nickel as the catalyst, it furnishes *tetrahydronaphthalene* (tetralin) and the *decahydride* (*v.* art. TETRALIN). When heated with amorphous phosphorus and hydriodic acid, it yields a *tetra-*, *hexa-*, *octo-*, or *deca- hydride* (*cf.* Graebe and Guye, Ber. 1883, 16, 3028); with sodium and ethyl alcohol a *dihydride* (Bamberger and Lodter, Annalen, 1895, 288, 75); and with sodium and amyl alcohol a *tetrahydride* (Bamberger and Kitschelt, Ber. 1890, 23, 1561).

On oxidation with potassium permanganate in aqueous solution (Tscherniac, D. R.-P. 79693; Procházka, Ber. 1897, 30, 3109; Graebe and Trümpy, Ber. 1898, 31, 369; Daly, J. Physical Chem. 1907, 11, 93) or, better, with potassium manganate (Tscherniac D. R.-P. 86914) naphthalene is converted into *phthalonic acid* with only a small proportion of *phthalic acid* (*cf.* Lossen, Annalen, 1867, 144, 71), but with acidified permanganate into *phthalic acid* (Tscherniac, *l.c.*) With nitric acid (sp.gr. 1·15) at 130°, *phthalic acid* is the product (Beilstein and Kurbatow, Annalen, 1880, 202, 215; *cf.* Boswell, J. Physical Chem. 1907, 11, 129); and with chromic acid mixture, *phthalic acid* (Lossen, *l.c.*) in 32 p.c. yield (Heller, Ber. 1912, 45, 674, footnote); but with chromic acid in acetic acid solution, [α-]*naphthaquinone* (Groves, Chem. Soc. J. 1873, 26, 209) and *phthalic acid* (Beilstein and Kurbatow, *l.c.*) are obtained. Oxidation in acid solution with ceric salts (Hochst, D. R.-P. 158609) or electrolytic oxidation (de Bottens, Zeitsch. Electrochem. 1902, 8, 673) in presence of cerous salts (Hochst, D. R.-P. 152063; Eng. P. 19178 of 1902) also converts it into [α]-*naphthaquinone* and *phthalic acid.* It is oxidised also, when heated with 15 times its weight of 100 p.c. sulphuric acid (monohydrate) and half its weight of mercuric sulphate at 200°, yielding *phthalic acid* in large amount, mixed with some *sulphophthalic acid* (Badische, D. R.-P. 91202; Eng. P. 18221 of 1896). Phthalic acid is also one of the products when its vapour is oxidised by air at 350°-500° in the presence of a catalyst such as vanadic oxide or vanadyl chloride (Selden Co. and Gibbs, Brit. P. 119518; Wohl, Brit. P. 145701; British Dyestuffs Corpn., (Green and Porter, Brit. P. 164785).

With chlorine, *naphthalene dichloride* (Fischer, Ber 1878, 11, 735, 1411), and *tetrachloride* (*q.v.*) are formed, which, by elimination of hydrogen chloride are converted into mono- and dichloronaphthalenes (Faust and Saame, Annalen, 1871, 160, 66; Krafft and Becker, Ber. 1876, 9, 1088; Widmann, Ber. 1882, 15, 2162; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 85). With bromine, it forms a *tetrabromide*, but only at low temperatures (Orndorff and Moyer, Amer. Chem J. 1897, 19, 262), and under ordinary conditions gives rise to substitution derivatives (Laurent, Ann. Chim. Phys. 1835, [ii.] 59, 216; Glaser, Annalen, 1865, 135, 40; Guareschi, Annalen, 1884, 222, 265; Armstrong and Wynne, *l.c.*)

Fuming nitric acid, or a mixture of nitric and sulphuric acids, converts naphthalene into *mono-*, *di-*, *tri-*, or *tetra-nitro-* derivatives; with sulphuric acid, according to the quantity, concentration, or temperature employed, *mono-*, *di-*, *tri-*, or *tetra-sulphonic acids* are formed.

When its vapour is passed through a red-hot iron tube, naphthalene yields about 15 p.c. of *ββ-dinaphthyl*, and, when mixed with ethylene, gives in addition a very small quantity of acenaphthene and phenanthrene (Ferko, Ber. 1887, 20, 662). Fusion with sodamide and phenol at 160°–220° converts it into a mixture of *α-naphthylamine* and 1 : 5-*diaminonaphthalene* (Sachs, Ber. 1906, 39, 3023).

Molecular compounds.—Naphthalene combines with trinitro-derivatives of benzene (Hepp, Annalen, 1882, 215, 380), toluene (Hepp, *l.c.*), aniline (Liebermann and Palm, Ber. 1875, 8, 377), phenol (Henriques, Annalen, 1882, 215, 332), or cresol (Noelting, Ber. 1882, 15, 1862; 1884, 17, 271), giving rise to crystalline molecular compounds of varying stability. Of these, the *compound* with picric acid, $C_{10}H_8+C_6H_2(NO_2)_3{\cdot}OH$, golden-yellow needles, m.p. 149°, dissolves in alcohol, ether, or benzene without decomposition and finds employment in methods for the estimation of the hydrocarbon (Fritzsche, Jahresb. Chem. 1857, 456); the *compound* with *s*-trinitrobenzene, $C_{10}H_8+C_6H_3(NO_2)_3$, forms pale yellow needles, m.p. 152·5° (Sudborough, Chem. Soc. Trans. 1916, 109, 1344).

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[1] According to Willstätter and Hatt (*l.c.*; *cf.* Willstätter and King, Ber 1913, 46, 534), the purest commercial naphthalene may contain as much as 0·25 p.c. of sulphur, which inhibits the action of the catalyst but may be removed by repeated crystallisation from alcohol.

Tests.—Commercial naphthalene should melt at 79°,[1] boil at 217°–218° at 760 mm., volatilise without leaving a residue, and be white and free from phenols or quinoline bases. When heated with concentrated sulphuric acid at 170°–200° it should at most colour the acid grey (Witt, Chem. Ind. 1887, 10, 216), or faintly purple, and when left in contact with nitric acid (sp.gr. 1·42) should remain white for at least half an hour (Lunge, Coal Tar and Ammonia, *l.c.*).

The presence of phenols can be detected by boiling the sample with dilute caustic soda solution, cooling, filtering, and adding to the filtrate bromine water and hydrochloric acid, when any phenols present will be precipitated in the form of brominated compounds. Quinoline bases are detected by dissolving the sample in warm concentrated sulphuric acid, pouring the solution into water, filtering, rendering the filtrate alkaline and distilling, when any quinoline bases present will pass over with the steam, and be recognised by their characteristic odour (Lunge, *l.c.*).

Estimation.—The proportion of naphthalene in commercial samples can be determined in many cases by sublimation. According to Kuster (Ber. 1894, 27, 1101) an acidimetric method, based on the formation of the insoluble picrate, can be used for determining naphthalene. In this process, a saturated solution of picric acid is employed, the excess of which is afterwards found by titration with standard baryta, using lacmoid as indicator; but as acenaphthene, chrysene and the naphthols also form insoluble compounds with picric acid, the method is valueless if they are present in the sample. In modified forms Küster's method has been employed for estimating the amount of naphthalene in coal gas (*cf. inter alia* Colman and Smith, J. Soc. Chem. Ind. 1900, 19, 128; Gair, *ibid.* 1905, 24, 1279; 1907, 26, 1263; Colman, Gas J. 1918, 144, 231).

Uses.— Until the discovery of the eosins about 1874, and of the azo- dyes about 1876, naphthalene was a waste product being either employed as a fuel, or burned for soot. Even now, production is in excess of the demand, although a considerable proportion of the output is utilised in the manufacture of phthalic acid, naphthylamines, naphthols and other important intermediates of the dyestuff industry.

To a limited extent it finds employment as a disinfectant and insecticide, and in the enrichment of gaseous fuels, but its use as a carburettor for coal gas in the albo-carbon burner has been abandoned as a consequence of the introduction of incandescent lighting (*cf. inter alia* Livesey and Kidd, D. R.-P. 2075; Eng. P. 244 of 1878; Kidd and Vale, Eng. P. 2135 of 1880; Vale, D. R.-P. 32255; Lunge, *l.c.*). Attempts made to convert it into liquid hydrocarbons for illuminating or lubricating purposes by alkylation, by hydrogenation under pressure, or by heating with aluminium chloride under pressure, have led only to unpromising results (*cf.* Fischer, Schneider, Hilpert, and Niggemann, Chem. Zentr. 1919, ii. 584) By its ready conversion into tetrahydronaphthalene (*tetralin*), however, a new opening has been found for it in the production of an oil which can be used as an illuminant, motor fuel, solvent or source of dyestuffs (*v.* art. TETRALIN). Certain synthetic tanning materials ('syntans'), produced from naphthalene to meet the shortage of natural tannins, have also the property in some cases of rendering soluble the insoluble part of the natural tanning agents.[2]

CONSTITUTION OF NAPHTHALENE AND NAPHTHALENE DERIVATIVES.

The naphthalene compounds of greatest technical importance in connexion with the manufacture of azo- dyes are the naphthylamines, naphthols, aminonaphthols, and the derived isomeric sulphonic acids. These substances are by no means equally valuable as sources of dyes; some, for example, do not couple with diazotised bases, or form only aminoazo- compounds, others yield azo- dyes which are not fast to soap, or are valueless on account of their shade, insolubility or instability,[3] and only a comparatively small number form azo- dyes which answer all the requirements of the dyer so far as fastness, tinctorial power, and delicacy of shade are concerned. A knowledge of the constitution of the naphthalene derivatives employed in the colour industry is thus of much importance, and it may be of interest to note that Patent specifications not infrequently contain the evidence on which constitutional formulæ adopted in this article have been assigned.

Constitution of naphthalene.—The Erlenmeyer-Graebe formula for naphthalene, proposed by Erlenmeyer (Annalen, 1865, 137, 346 (footnote)), but first made probable on the basis of experimental evidence by Graebe (Annalen, 1869, 149, 22), represents the molecule as composed of two six-membered rings having two carbon atoms in common. This arrangement is shown in formula I, with which formula II, or, conventionally, when the object is merely to show the relative position of substituents in the molecule, formula III is equivalent:—

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[1] In practice, the temperature at which the sample solidifies is preferred to the melting-point, the determination, if made in Shukoff's apparatus, being accurate to 0·1° (Chem. Zeit. 1901, 25, 1111).

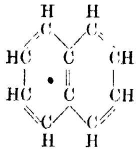
[2] For the preparation of these materials, formaldehyde is condensed with naphthalenemonosulphonic acids (*v.* p. 422), or with *a*- or *β*-naphthylaminesulphonic acids (Deutsch-Kol Gerb- u Farbstoff-Ges., D. R.-P. 293041, 293640, 294825, 315871. Durand and Huguenin, Brit. P. 138796) or with *a*- or *β*-naphtholsulphonic acids (Deutsch-Kol Gerb- u Farbstoff-Ges, D. R.-P. 293042, 293693, 305795, 306132; Badische, D. R.-P. 291457). Those from the naphthols give colour reactions with ferric chloride and couple with diazotised bases.

[3] For example. each of the following acids (2 mols.) coupled with diazotised benzidine (tetrazodiphenyl) gives worthless azo-dyes of the shades indicated:—

(*a*) *β*-Naphthylaminesulphonic acids: 5-[*γ*-]acid, sparingly soluble orange-yellow; 6-[*β*-]acid, insoluble reddish-brown; 7-[*δ*- or F-]acid, red changing to brown by action of atmospheric carbon dioxide; 8-[*a*-] none, but a yellow diazoamino- compound;

(*b*) *β*-Naphthylaminedisulphonic acids: 3 : 6-[amino-R-]acid, red of little tinctorial power; 6 : 8-[*γ*- or amino-G-] acid, yellow and fugitive.

On the other hand, *β*-naphthylamine-3 : 7-disulphonic acid gives a red dye, remarkably fast towards light and acids (Cassella, D. R.-P. 46711).



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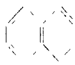

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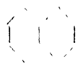
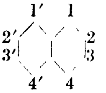
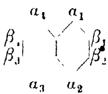


III

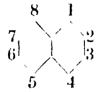
To save the labour of writing the symbol each time it is desired to indicate the orientation of a substituent, several methods for distinguishing the positions have been devised, of which three are shown in the symbols IV–VI.—



IV



V



VI

Of these the last (VI), originally proposed by Graebe in 1869, and adopted by the Geneva Congress on Nomenclature in 1892 (Chem. News, 65, 280), is the only one now in use.

With one exception (Wreden, Ber. 1876, 9, 950) all the formulæ proposed for naphthalene [1] show two six-membered rings in the same plane,[2] but differ from one another, and from the Erlenmeyer-Graebe symbol, in the mode of distribution of the fourth valency of each carbon atom, on which the unsaturation of the molecule, and the properties distinguishing naphthalene compounds from those of benzene probably depend. These six-membered rings have been termed benzene or benzenoid rings, but under a misapprehension: neither ring has the properties of benzene until the unsaturation of the other has been destroyed.

The determination of the relative positions of substituents in the molecule depends, as in the case of benzene, on considerations arising out of the formula itself. Provided the substituents are all alike, the number of mono-, di-, and tri-derivatives of naphthalene, deducible from the Erlenmeyer-Graebe symbol, is 2, 10, and 14 respectively. Investigation of all the substances described in the literature as dichloro- and trichloro-naphthalenes has shown that the number is ten for the one and fourteen for the other,[3] in agreement therefore with the number of isomerides predicted from the formula (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 77; 1895, 11, 84). In no other series of tri-derivatives have all the possible isomerides been isolated, but as, by well-known reactions, it is not difficult in most cases to connect a naphthalene derivative under investigation with one of the chloronaphthalenes, this group of substances serves as a standard to which the orientation of other di- and tri- derivatives is referred.

In the tables which follow, the melting-points and crystalline appearance of the dichloro- and trichloro-naphthalenes are given, but as these may not in every case be sufficient for characterisation, the respective sulphonic acids (each of which furnishes a chloride and amide of definite melting-point) can be utilised to render identification complete.

Dichloronaphthalenes.

Trivial name	Constitution	Melting-point	Character of crystallisation from alcohol
—	1 . 2	35°	Prisms.
—	1 . 3	61°	Long, flat needles
[β-]	1 . 4	67·5	Long, flat needles.
[γ-]	1 . 5	107°	Short, flat needles
[η-]	1 . 6	48	Long, flat needles.
[θ-]	1 . 7	62·5°	Small aggregates.
[ξ-]	1 . 8	82°	Rhombohedra
[ι-]	2 . 3	119·5°	Thin, lustrous scales.
[ε-]	2 . 6	135°	Long, flat needles.
[δ-]	2 . 7	114°	Thin laminæ.

Trichloronaphthalenes.

Trivial name	Constitution	Melting-point	Character of crystallisation from alcohol
[α-]	1 . 2 . 3	81°	Groups of long needles.
—	1 . 2 . 4	92°	Tufts of flat needles
—	1 . 2 . 5	78·5°	Short, flat needles.
—	1 . 2 . 6	92·5°	Slender needles
—	1 . 2 . 7	88° and 84°	Microscopic needles.
—	1 . 2 . 8	83·5°	Long slender needles.
[γ-]	1 . 3 . 5	103°	Long, flat needles
[θ-]	1 . 3 . 6	80·5°	Tufts of thin needles.
[η-]	1 . 3 . 7	113°	Short, thin needles.
[β-]	1 . 3 . 8	89·5 and 85°	Large, flat prisms.
[δ-]	1 . 4 . 5	131°	Very long needles.
[ε-] and [ζ-]	1 . 4 . 6	66° and 56°	Needles, becoming opaque
—	2 . 3 . 5	109°	Long, thin needles.
—	2 . 3 . 6	91°	Minute plates.

Throughout this article the constitution of a substance is indicated by numerals, except in those cases where the use of α- and β-, as equivalent to the 1- and 2- positions, is commonly employed, *e.g.* α-naphthol instead of the less familiar 1-hydroxynaphthalene. When it has been necessary to use the letters α-, β-, γ- . . . to distinguish isomerides without reference to constitution, whether known or unknown, the plan adopted by Ladenburg (Handwörterbuch, art. NAPHTALIN) of placing them in brackets (*e.g.* [α-]) has been followed.

SUBSTITUTION IN THE NAPHTHALENE SERIES.

A full discussion of the laws of substitution in the naphthalene series, and of the theories which have been proposed to account for or explain them, lies outside the scope of this article, but a summary of what is known or surmised in connexion with the course which substitution follows during nitration and sulphonation may be attempted in view of the importance of these processes in the manufacture of naphthalene derivatives for use in the colour industry.

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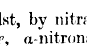
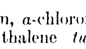
[1] *Cf.* Berthelot, Compt. rend. 1866, 63, 788, 834; Wichelhaus, Ber. 1869, 2, 197; Wreden (second formula), *l.c.*; Claus, Ber. 1882, 15, 1827; Bamberger, Annalen, 1890, 257, 44; Armstrong, Chem. Soc. Proc. 1890, 6, 102; Thiele, Annalen, 1899, 306, 138; Knoevenagel, *ibid.* 1900, 311, 194; Hartley, Chem. Soc. Trans. 1905, 87, 1828; Baly and Tuck, *ibid.* 1908, 93, 1905; Willstätter and Waser, Ber. 1911, 44, 3423; Willstätter and Hatt, Ber. 1912, 45, 1481; Bamberger, Ber. 1913, 46, 1899; J. J. Thomson, Phil. Mag. 1914, [vi] 27, 784; Weinberg, Ber. 1921, 54, 2170; W. H. Bragg, Phys. Soc. Proc. 1921, 34, 42.

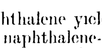
[2] Kaufler (Annalen, 1907, 351, 154) has proposed a formula with the two rings in different planes.

[3] When the substituents are not alike the number of isomerides is greater; thus the possibility that 14 naphtholsulphonic acids, 42 naphtholdisulphonic acids, and 84 aminonaphtholsulphonic acids may exist is deducible from the naphthalene symbol.

The existence of two series of mono- substitution derivatives in the naphthalene series, and the fact that substitution tends to occur mainly in the α- position have long been recognised For example, by chlorination, bromination or nitration, naphthalene yields α-chloro-, α-bromo- or α-nitro-naphthalene ;







whilst, by nitration, α-chloronaphthalene yields *three*, α-nitronaphthalene *two*, naphthalene-α-sulphonic acid *three*, and naphthalene-β-sulphonic acid *three* α-nitro- derivatives. Owing to the very small proportion in which the β-isomeride is formed, the presence of β-chloro- and β-bromo- naphthalene in the respective mono- substitution products escaped recognition until comparatively recently, and that of β-nitro- in α-nitro-naphthalene is still a matter of dispute

With sulphuric acid as the agent very different results are obtained. Faraday, who was the first to study the action of sulphuric acid on naphthalene, isolated the barium salts of the two monosulphonic acids, known now as the α- and β- acids, and later investigations have not only confirmed his discovery, but shown that the β compound increases in amount as the temperature of sulphonation is raised until at 160° it constitutes almost the sole product. This increase in the amount of the β-, accompanied by a corresponding diminution in that of the α- acid, is shown clearly by the following numbers, obtained with many others by Euwes in a quantitative study of the molecular reaction expressed by the equation :—

$$C_{10}H_8+H_2SO_4 \rightarrow C_{10}H_7SO_3H+H_2O$$

In his experiments, monohydrate was the acid used and 8 hours the duration of the heating (Rec. trav. chim. 1909, 28, 298) :—

t°	Per cent of $C_{10}H_8$ recovered[1]	Per cent. in product of		Sulphone per cent
		α-acid	β-acid	
80°	27·0	96·4	3·6	—
100°	20·0	83·2	16·8	—
129°	10·0	44·4	55·6	1·0
138·5°	8·6	28·4	71·6	(?)
150° [2]	6·4	18·3	81·7	3·2

According to Euwes, when equilibrium is attained, the relative proportion of α- and β-acid is fixed for any given temperature; thus with 90 p.c., 96 p.c., and 100 p.c. sulphuric acid at 129°, the proportion of α-acid in the product was 44·6–44·4 p.c., the recovered naphthalene being 32 p.c., 23 p.c., and 10 p.c. respectively. That equilibrium is attained by the gradual replacement of α-acid by β-acid was made evident by shortening the duration of the reaction; thus, at 129°, all other conditions being unchanged, the melt at the end of 35 minutes contained 79 p.c. of α-acid, but at the end of 6 hours only 45 p.c.

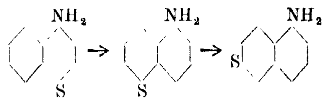
It has long been known that sulphonation is a reversible process, and, in the naphthalene series that α-sulphonic acids are hydrolysed at lower temperatures than β-sulphonic acids under conditions otherwise comparable. To Noelting is due the suggestion that naphthalene, regenerated by hydrolysis of its α-sulphonic acid at the high temperature is at this high temperature resulphonated, but in the β-, not the α- position (Ber. 1875, 8, 1095). This explanation, which does not account for the presence of β-acid in the product formed even at so low a temperature as 0° (*cf.* Fierz and Weissenbach, Helv. Chim. Acta, 1920, 3, 314) or for its progressive increase as the temperature rises, seems to have been accepted (*cf.* Weinberg, Ber. 1887, 20, 3354; Bender, Ber. 1889, 22, 994) until Erdmann published the first detailed study of an example of sulphonation (Annalen, 1893, 275, 192)

Briefly, Erdmann's results, which were obtained with α-naphthylamine, showed that :—

(i.) When heated with 5 times its weight of 95–96 p c. sulphuric acid at 130°, the base was rapidly converted into the 4-sulphonic acid, with a small amount of the 5-sulphonic acid and traces of the 6-sulphonic acid :

(ii.) The product at the end of 20 minutes was soluble in water, but contained some α-naphthylamine ;

(iii.) The amount of naphthylamine increased, with simultaneous formation of the 4 : 7-disulphonic acid, as the heating at 130° was prolonged, the 5-sulphonic acid, and afterwards the 6-sulphonic acid, becoming the chief product :



To explain these facts, Erdmann modified Noelting's view by the assumption that the 4-, 5-, and 6-sulphonic acids are produced simultaneously but in widely differing amounts. The formation of water by the further sulphonation of the naphthylamine-4-sulphonic acid

$$NH_2\,C_{10}H_6\,SO_3H+H_2SO_4=NH_2\,C_{10}H_5(SO_3H)_2+H_2O$$

disturbs the equilibrium which otherwise would be attained, and brings about the hydrolysis first of the 4-sulphonic acid, and then of the 5-sulphonic acid. Thus he accounted for the increase in the amount of α-naphthylamine; of the 5-sulphonic acid; and finally of the 6-sulphonic acid—the least easily hydrolysed of the three acids—in the product.

In a re-investigation of the sulphonation of β-naphthylamine, Green and Vakil obtained results (Chem. Soc. Trans. 1918, 113, 35; *cf.*

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[1] It should be noted that this decrease in the amount of naphthalene recovered at the higher temperatures does not harmonise with Merz and Weith's results (*v. Naphthalene-α-sulphonic acid*).

[2] At temperatures above 160°, disulphonic acid was formed, but the data given do not show to what extent, if any, the consequent increase in dilution of the sulphuric acid influenced the relative proportion of α- and β-monosulphonic acids.

Green, *ibid.* 1889, 55, 33) which may be summarised as follows :—

(i.) When β-naphthylamine was heated with 4 times its weight of 96 p.c. sulphuric acid at temperatures between 40° and 120°, and for periods varying between 5 and 25 hours, the product in each case contained the four heteronuclear sulphonic acids. The table gives the relative proportion of these acids in four melts selected from among those examined :—

$t°$	Duration in hours	8-acid p c	5-acid p c	Mixed 6- and 7-acids p c
40°	5	38	61·6	0·4
80°	5	44	55·3	0·7
80°	20	36	61·6	2·4
120°	5	26	66·5	7·5

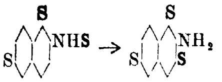
(ii.) With 60 p.c. sulphuric acid the facility with which the isomeric acids were hydrolysed could be expressed thus : 2 : 8 > 2 : 5 > 2 : 6 and 2 : 7.

(iii.) The 8-sulphonic acid was replaced by the 5-sulphonic acid in amounts varying from about 20 p.c. with 80 p c. sulphuric acid at 80° to about 43 p.c. with 90 p.c. acid at 120° during 10 hours, but not the 5- by the 8-acid.

Reviewing these results they conclude that sulphonation of β-naphthylamine takes place initially and simultaneously in the 8- and the 5-positions, the proportion being fixed for any particular temperature ; further, that with rise of temperature or by prolongation of the reaction, the 8-sulphonic acid is hydrolysed regenerating β-naphthylamine, which is resulphonated furnishing a mixture of the 8- and 5- sulphonic acids as before, and so on.

While Erdmann's view accounts for the phenomena observed in the above and in similar cases of sulphonation, being based on the assumption that the introduction of a sulphonic group, like that of other substituents, takes place mainly in α- and only to a small extent in β- positions at whatever temperature it may be effected—the subsequent change in the proportion of the isomerides being due to hydrolysis mainly of α-acid and resulphonation —it does not furnish a general theory of sulphonation. For example, it leaves unexplained :

(*a*) The transference of the SO_3H radicle **S** to a β-position under the influence of 30–40 p.c. anhydrosulphuric acid at 130°–180° in such cases as the following : [1]

I.


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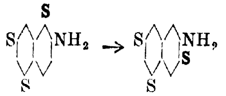

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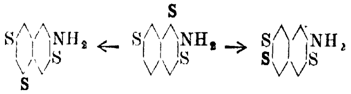
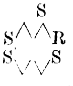
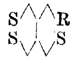


(*b*) The infrequency of sulphonation in contiguous $\alpha\beta$- or $\beta\beta$- positions and the fact that sulphonic acids in which the SO_3H radicles occupy relatively the 1 : 4- or the 1 : 8 positions, although obtainable by indirect methods (*v* p. 421) have never been isolated from or detected in a sulphonation melt even when on general grounds their presence might have been anticipated.

Sulphonation in contiguous positions is known to occur only in five cases and in each it is effected by the aid of 40 p.c. anhydro-acid at 130°. Four of the products are the β-naphthylamine- and β-naphtholsulphonic acids of the orientation [R being NH_2 or OH] :—





in which the contiguity is found in $\beta\beta$- positions, and the fifth is an α-naphthasultamtrisulphonic acid, in which it occurs either in a $\beta\beta$- or in an $\alpha\beta$- position.

Laws of Substitution in the Naphthalene Series.

Reference has been made to the fact that monosubstitution occurs mainly in the α-position. When a second radicle enters the molecule it may do so in the same ring as the first—homonucleally—or in the other ring—heteronucleally. As in the case of benzene, it is possible to indicate in general terms the directing influence of the radicle already present in the naphthalene molecule on the position taken up by the entering substituent, but a comparison of the laws of substitution deduced for the two series, benzene and naphthalene, shows important differences. Considered only with reference to the naphthalene derivatives which find a place in this article and to the production of disubstitution derivatives, the following generalisation can be made :—

Homonuclear substitution occurs in position 4, or in positions 2 and 4—

(i.) When Cl, OH, or NHAc [2] is already present in the α- position ;

but in position 1, or in positions 1 and 4—

(ii.) When OH or NHAc is already present in the β- position.

Heteronuclear substitution occurs in position 5, or in positions 5 and 8—

(i.) When NO_2 or SO_3H is already present in either the α- or the β- position.

(ii.) When Cl or NH_2 is already present in the β- position.

The position taken initially by the entering substituent in the ring is also the final position, except in the case of sulphonation in which, if the conditions are favourable, β-sulphonic acids may replace the α-sulphonic acids first produced (*v.* p. 413).

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[1] Until their nature and the operative conditions are better understood, changes of this type can be classified only as intramolecular or isomeric. Apart from the many cases of 'isomeric change' among sulphonic acids, two others are sufficiently remarkable to merit reference, *viz* the conversion of naphthalene-α-sulphohydroxamic acid $C_{10}H_7 \cdot SO_2 \cdot NH \cdot OH$ into naphthalene-β-sulphinic acid and of dinaphthalene-α-sulphohydroxamic acid $(C_{10}H_7 \cdot SO_2)_2N \cdot OH$ into the β-compound by dilute alkali solutions at the ordinary temperature (Angeli, Angelico and Scurti, Gazz. chim. ital. 1903, 33 ii, 296).

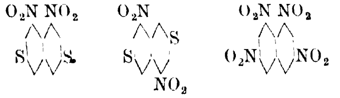
[2] Reference to α-naphthylamine derivatives will show that a summary of the directing influence of the NH_2 radicle in α-compounds cannot easily be made.

Although the orientation of trisubstitution derivatives cannot be predicted with any great approach to accuracy from a knowledge of the constitution of the di-derivative employed, yet from the facts accumulated about nitration and sulphonation, two deductions can be drawn :—

(i.) The non-existence in the sulphonation melt of derivatives in which SO_3H groups occupy relatively the 1 : 2-,[1] 1 : 4-, or 1 : 8-positions, has its counterpart in the rare occurrence of nitro- compounds containing NO_2 groups relatively in the 1 : 2- or 1 : 4- positions. The analogy does not extend to the 1 : 8- positions, many 1 : 8- dinitro- derivatives being known.

(ii.) The inhibition of 1 : 2-disulphonation and largely of 1 : 2- dinitration extends to the sulphonation of nitro- compounds, and to the nitration of sulphonic acids. No case is known in which a NO_2 and a SO_3H group occupy relatively the 1 : 2- or the 2 · 1- positions.

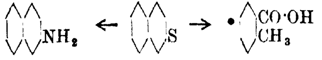
As an illustration of the effect of these restrictions on the orientation of nitration products, the constitution of the following substances, said to be the only dinitration products of naphthalene-2 : 6- and 2 : 7-disulphonic acids, and of 1 : 8-dinitronaphthalene, may be quoted :



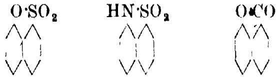
Properties peculiar to 1 : 3- *and* 1 : 8- *Derivatives.*

While the properties of the 1 : 2- and 1 : 4- derivatives of naphthalene resemble, in the main, those of the corresponding *ortho-* and *para-* derivatives of benzene, there is no such agreement between the properties of 1 : 3-derivatives in the two series. For this reason the use of the prefix *meta-* for naphthalene compounds of this orientation is apt to be misleading. Moreover, from the point of view of substitution, it is evident (*v. supra*) that the 5- and 8- positions, more nearly than the 3-position, in naphthalene have the functions of the *meta-* position in benzene.

As examples of properties peculiar to di- (and tri-) derivatives of naphthalene containing the radicles OH, NH_2, or SO_3H relatively in the 1 : 3 positions, reference may be made to the conversion of α-naphthol- or α-naphthylamine-3-sulphonic acid [2] into 1 : 3-diaminonaphthalene by interaction with ammonia, and into *o*-toluic acid by fusion with caustic potash.



Turning to 1 : 8- or *peri-* derivatives, certain of these furnish internal condensation products, *e.g.* naphthalic anhydride, recalling the behaviour of some 1 : 2- or *ortho-* derivatives under similar conditions. But, as condensation in each of these positions is dependent on the possibility of a 5- or 6- membered ring being formed, many of the products arise from reactions applicable only to the one series or the other, but not to both. For example, among the well-known *ortho-* condensation products, anhydrides of the following types obtained with *peri-* derivatives are not represented :



Sultone. Sultam. Lactone.

The Bisulphite Reaction.

α-Nitronaphthalene, on reduction in an acid medium, furnishes α-naphthylamine. Piria found that when aqueous alcoholic ammonium sulphite is employed the products are α-naphthylamine-sulphamic (thionaphthamic) and 4-sulphonic acids (Annalen, 1851, 78, 31). For more than forty years this discovery remained an isolated fact, although the interest attaching to the reaction is considerable, as the conversion of α-naphthylamine into the 4-sulphonic acid by the usual method requires both concentrated sulphuric acid and a high temperature.

From the patents of Fischesser (D. R.-P. 76438 : 79577), it is evident that the method is of restricted application, but can be used for the simultaneous reduction and sulphonation of α-nitronaphthalene-3 : 8-disulphonic acid, and of 1 : 5-dinitro- or (*cf.* Höchst, D. R.-P. 215338) of 1 : 8-dinitro-naphthalene by the aid of sodium bisulphite solution. Further, α-nitronaphthalene with a large excess of bisulphite yields not Piria's compounds, but α-naphthylamine-2 : 4-disulphonic acid [3] (Höchst, D. R.-P. 92082).

In none of these cases is the nitrogen atom eliminated from the molecule as the result of the interaction with bisulphite, but in the last recorded application of the process—conversion of 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid into 1-amino-8-naphthol-3 : 6-disulphonic acid (Bayer, D. R.-P. 113944 ; *cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 349)– replacement of a NO_2 (or NH_2) group by OH was observed, and a new field for investigation opened up.

Slightly earlier in date than this patent of Bayer & Co., is one in which it is shown that the conversion of amino- into hydroxy- derivatives in the naphthalene series can be achieved under the influence of sodium bisulphite solution in open vessels at the boiling-point (Bayer, D. R.-P. 109102).[4] With β-naphthylamine derivatives, unless a large excess of bisulphite is used (Badische, D. R.-P. 134401 ; *cf.* Bucherer and Stohmann, J. pr. Chem. 1905, [ii.] 71, 436), condensation to ββ′-dinaphthylamine derivatives occurs (Bayer, D. R.-P. 121094).

The clue to these results was supplied by

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[1] Naphthasultamtrisulphonic acid (*q.v.*) is a possible exception.

[2] The β-naphthol- and β-naphthylamine-4-sulphonic acids yield the toluic acid but not the diamine.

[3] Bucherer (J. pr Chem 1904, [ii.] 69, 50) makes the interesting statement that occasionally a small quantity of α-naphthol-4-sulphonic acid is formed in this reaction.

Two nitroso compounds, α-nitroso-β-naphthol and β-nitroso-α-naphthol, also undergo this type of change with sodium bisulphite solution, furnishing the corresponding aminonaphtholsulphonic acids (Böniger, Ber. 1894, 27, 23)

[4] This discovery is now credited to Lepetit (*cf.* Friedlander, Ber. 1921, 54, 620), but the application of the reaction to the production of amino- and arylamino-naphthalene derivatives and its detailed study, including the recognition of its reversible nature, is due to Bucherer.

Bucherer's discovery that in this reaction a highly soluble intermediate compound is formed, which, although stable towards acids, is decomposed by alkalis with the production of ammonia and the naphthol.[1] This intermediate compound was considered to be an ester, identified as *a*- or *β*-naphthyl sulphite $C_{10}H_7{\cdot}O{\cdot}SO_2Na$ (Badische, D. R.-P. 126136) as it does not couple with diazotised bases, can be obtained from the corresponding naphthol by interaction with bisulphite (Badische, D. R.-P. 115335), and regenerates the naphthylamine by interaction with ammonia, the yield of *β*-naphthylamine from *β*-naphthol being almost quantitative (Badische, D. R. P. 117471; Bucherer, J. pr. Chem. 1904, [ii.] 69, 88). By the use of methylamine, aniline or their homologues in place of ammonia, alkylated *a*- and *β*- naphthylamines (Badische, D. R.-P. 121683) and arylated *β* naphthylamines (Badische, D. R.-P 122570) can be obtained.[2]

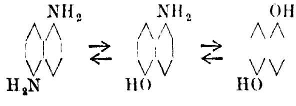
In the patent literature and in the papers published by Bucherer (J. pr. Chem. 1904, [ii.] 69, 47; 70, 345; 1905, [ii.] 71, 433), the following convenient expression for the bisulphite reaction is given, which shows clearly the reversible nature of the change —

$$RN{}^{R_1}_{R_2}\ \underset{+NHR_1R_2}{\overset{+\text{bisulphite}}{\rightleftarrows}}\ RO\cdot SO_2H\ \underset{+\text{bisulphite}}{\overset{+\text{alkali}}{\rightleftarrows}}\ R{\cdot}OH$$

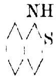
R being a naphthyl radicle and R_1R_2 hydrogen, alkyl, or (for *β*- compounds only) aryl radicles.

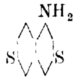
In practice, if a hydroxy- compound is to be prepared, the corresponding amino- derivative is digested with excess of 40 p.c. sodium bisulphite solution usually at 80°–90° until a test shows the reaction to be complete, the product boiled with caustic alkali solution to expel ammonia, and then acidified to remove sulphurous acid. If, on the other hand, the reverse process is to be followed, then the hydroxy-compound is digested with excess of 20–40 p.c. ammonium sulphite solution and 20 p.c. ammonia in an autoclave provided with a stirrer at 100°–150° until conversion is complete, and the product afterwards acidified.

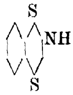
With the exception of derivatives of *m*-dihydroxy- and *m*-diamino-benzene the bisulphite reaction is confined to the naphthalene series, and is dependent on the use of a large excess (3–5 mols.) of the reagent. It is applicable to diaminonaphthalene, aminonaphthol and dihydroxynaphthalene derivatives as well as to the naphthylamines and naphthols,



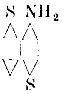
its technical importance being therefore evident. But it is subject to restrictions; for example, it does not succeed with *a*- derivatives in which a substituent is present in the 2- or 3- position, or with *β*- derivatives in which a substituent is present in the 4- position, such as the acids:

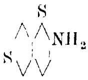


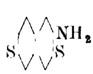




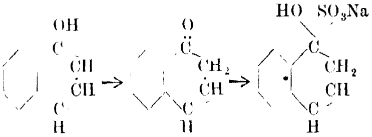
although it takes place easily with acids in which these respective positions are not occupied:







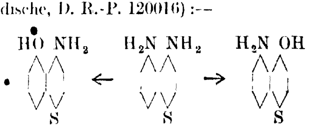
Bucherer's view of the nature of the intermediate product throws no light on the cause of these restrictions. If, however, it be assumed that the reaction proceeds not by the formation of a sulphite ester from the stable naphthol (enol) but of an additive bisulphite product from the tautomeric ketodihydronaphthalene (ketone)



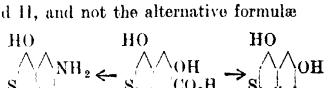
the marked reactivity towards primary amines will accord with expectation and the restrictions admit of explanation on steric grounds (*cf.* Vorosheov, Chem Soc. Abstr. 1916, 110, i, 293; Chem. Zentr. 1916, II, 256; Friedlander, Chem Zeit 1916, 40, 919; Ber 1921, 54, 620; König and Haller, J. pr. Chem. 1920, [ii.] 101, 43).

Many interesting applications of the reaction are to be found in the literature, from which two may be taken by way of illustration:

(*a*) 1·8-Diaminonaphthalene-4-sulphonic acid will furnish either the 4- or the 5-sulphonic acid of 1-amino-8-naphthol according as the process is conducted in the presence or absence of acetone (Badische, D. R.-P. 120016):—



(*b*) Two formulæ are possible for the aminonaphtholsulphonic acid, and two for the dihydroxynaphthalenesulphonic acid obtained respectively by fusing *β*-naphthylamine- and *β*-naphthol-6:8-disulphonic acids with caustic potash. That these acids have the formulæ I and II, and not the alternative formulæ



I Nigrotic acid II

is established by the fact that they can also be formed from nigrotic acid by digestion with ammonium sulphite and with sodium bisulphite solutions respectively. Carbon dioxide is eliminated in both cases, and formula I follows from what is known of the restrictive effect exercised by the SO_3H group on the reactivity of the OH radicle to which it stands relatively in the 3-position in the same nucleus (Bucherer and Seyde, J. pr. Chem. 1907, [ii.] 75, 254).

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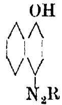
[1] This process differs essentially from that in which the exchange of NH_2 for OH is effected at high temperatures under the influence of water or mineral acids (*cf.* however, Franzen and Kempf, Ber 1917, 50, 101). The end products of the two reactions are usually the same, but differences between them are not unknown, *e.g.* *a*-naphthylamine-4-sulphonic acid is converted almost quantitatively by the bisulphite method into *a*-naphthol-4-sulphonic acid, but by the acid method into *a*-naphthol.

[2] With phenylhydrazine, the reaction proceeds differently leading to the formation of 1:2-phenocarbazole-N-sulphonic acids as chief products (Bucherer and Seyde, J. pr. Chem. 1908, [ii.] 77, 403; D. R.-P 208690).

DIAZO- AND AZO- COMPOUNDS.

Without exception, diazotised bases couple homonucleally with naphthols, naphthylamines, aminonaphthols or their sulphonic acids.[1] Stated in general terms, α-hydroxy- and α-amino-naphthalene derivatives couple in the 4- or *para-* position (I), as is the case with benzene derivatives, but when this position is occupied by a radicle other than hydrogen, also couple readily in the 2- or *ortho-* position (II) relatively to the OH or NH_2 group. In the β-series of compounds, there being no *para-* position available, coupling invariably takes place in the *ortho-* position relatively to the OH or NH_2 group, but with this limitation that the entering diazo- group assumes the 1- position (III) to the exclusion of the 3- position, although both the 1 : 2- and the 3 : 2- positions are contiguous and to that extent comparable with the *ortho-* position in the benzene molecule. It is obvious, therefore, that the 3- position, in comparison with the 1- position, is passive in this type of chemical change: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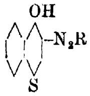
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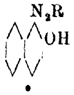
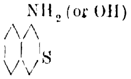
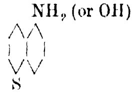

III

To this generalisation there are exceptions among amino- and hydroxy-naphthalenesulphonic acids of certain configurations, of which two may be noted:

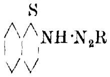
(i.) α-Naphthylamine- or α-naphthol-sulphonic acids of the formulæ:

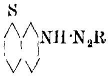




couple in the 2- position, although in none of them is the 4- position occupied (Gattermann and Schulze, Ber. 1897, 30, 50). This rule, however, is not always followed when the diazotised base contains a negative substituent in the *ortho-* or *para-* position. Thus, diazotised *p*-nitraniline couples with α-naphthylamine-3-sulphonic acid in the 2- position and with α-naphthol-5-sulphonic acid in the 4- position, but with α-naphthylamine-5- and α-naphthol-3-sulphonic acids in both the 2- and the 4- positions (Gattermann and Liebermann, Annalen, 1912, 393, 200).

(ii.) β Naphthylamine-8-sulphonic acid and its derivatives, like the 1- sulphonic acids, furnish diazoamino- compounds instead of azo- derivatives:





Other cases of deviation from the general rule will be found among sulphonic acids of the diaminonaphthalenes, aminonaphthols, and dihydroxynaphthalenes.

Coupled in the *ortho-* position, naphthylamines, naphthols and their sulphonic acids furnish valuable dyestuffs which are fast to soap, but in the *para-* position, peculiar to α- compounds, they give products which are almost useless as dyes, changing colour as they do when brought in contact with acids and alkalis. But while, in the *ortho-* amino-azo-dyes, the amino-group cannot be diazotised, the *para-* amino-azo-dyes are themselves readily diazotisable and find extensive use in the production of dyestuffs containing an additional azo- group. α-Naphthylamine and certain of its sulphonic acids, particularly the 6- and 7-sulphonic acids, are largely used as middle components, but the β- derivatives only as end components in azo-dyestuff manufacture.

The position of the azo- group in azo- dyes can be determined either by reduction, *e.g.* with stannous chloride (Witt, Ber. 1888, 21, 3471), or with sodium hypo- ('hydro-') sulphite (Grandmougin, Ber. 1906, 39, 2494, 3561, 3929), whereby the base used for diazotisation and an amino- derivative of the second component are obtained; or by fission with cold fuming nitric acid (Schmidt, Ber. 1905, 38, 3202; *cf.* Meldola and Hanes, Chem. Soc. Trans. 1894,

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[1] The following trivial names are given to sulphonic acids employed in the manufacture of azo-dyes:—

Naphthylaminesulphonic acids [$NH_2 \cdot SO_3H$]
[1 : 4] Naphthionic
[1 : 5] Laurent
[1 8] S or Schollkopf
[2 . 6] Bronner
[2 · 7] F-acid
[2 . 8] Badische

Naphthylaminedisulphonic acids [$NH_2 : SO_3H \cdot SO_3H$]
[1 : 3 : 8] ε-disulpho
[1 : 4 . 8] Disulpho S
[2 3 : 6] Amino-R
[2 : 3 . 7] Disulpho F
[2 : 4 8] Disulpho C
[2 . 6 . 8] Amino-G

Naphtholsulphonic acids [$OH : SO_3H$]
[1 : 4] Nevile & Winther
[1 : 5] L-acid
[1 : 8] S-acid
[2 6] Schäffer
[2 7] F-acid
[2 . 8] Crocein-acid

Naphtholdisulphonic acids [$OH . SO_3H \ SO_3H$]
[1 : 3 8] Disulpho E
[1 . 4 : 8] Disulpho. S
[2 . 3 · 6] R-acid
[2 3 . 7] F-acid
[2 . 4 . 8] C-acid
[2 · 6 . 8] G-acid

Aminonaphtholsulphonic acids [$NH_2 \ OH \ SO_3H$]
[1 · 5 : 7] M-acid
[1 : 7 : 3] B-acid
[1 . 8 . 4] S-acid
[1 : 8 : 6] H-monosulpho.
[2 · 3 . 6] R-acid
[2 . 5 : 7] J-acid
[2 7 : 3] F-acid
[2 : 8 : 6] G-acid
[2 : 8 ?] V-acid

Aminonaphtholdisulphonic acids [$NH_2 \cdot OH : SO_3H : SO_3H$]
[1 : 8 : 2 : 4] S-acid
[1 . 8 . (2) : ?] L-acid
[1 : 8 · 3 : 5] B-acid
[1 : 8 : 3 . 6] H-acid
[1 : 8 · 4 · 6] K-acid
[1 . 8 (5) . ?] D-acid
[2 . 8 3 : 6] 2R-acid

Dihydroxynaphthalenesulphonic acids [$OH : OH : SO_3H$]
[1 : 5 : 2] C-acid
[1 : 7 : 3] G-acid
[1 : 8 : 3] ε-acid
[1 : 8 : 4] S-acid
[2 : 3 · 6] R-acid
[2 . 7 : 3] F-acid

Dihydroxynaphthalenedisulphonic acids [$OH : OH : SO_3H : SO_3H$]
[1 : 3 : 5 : 7] Yellow acid (Gelbsäure)
[1 : 5 : 3 : 7] Red acid (Rotsäure)
[1 : 7 : 3 : 6] A-acid
[1 : 8 : 2 : 4] S-acid [1 . 8 : ? · ?] I-, G-, and R-acids
[1 : 8 : 3 : 5] K-acid [2 : 3 : 6 : 8] B-acid
[1 : 8 : 3 : 6] Chromotrope acid

Dihydroxynaphthalenecarboxylic acids [$OH : OH : CO_2H$]
[1 : 7 : 6] S-acid
[2 : 6 : 3] L-acid

Carbodihydroxynaphthalenesulphonic acid [$OH : OH : CO_2H : SO_3H = 1 : 7 : 6 . 3$] Nigrotic acid.

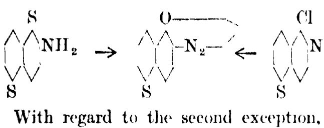
65, 841), whereby the diazo- compound used and a nitro-derivative of the second component are formed. The former of these processes has found some application in the preparation of aminonaphthalene derivatives (*v. Diaminonaphthalene-* and *aminonaphthol-sulphonic acids*).

Diazo-oxides.—The formation of diazo- compounds by interaction of naphthylamine- or aminonaphthol-sulphonic acids with nitrous acid proceeds normally except with :—

(*a*) Naphthylaminesulphonic acids containing one SO_3H group in the *ortho-* (1- or 2-) position relatively to the amino- radicle ;

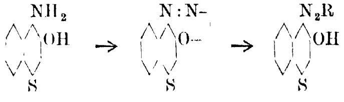
(*b*) 1 : 2- and 2 : 1-aminonaphtholsulphonic acids or their derivatives.[1]

With respect to the first exception, it is found that when warmed with solutions of alkali carbonates or acetates, to remove free mineral acid, diazotised *α*- or *β*-naphthylamine-*ortho*-sulphonic acids (Badische, D. R.-P. 145906 ; Eng. P. 6615 of 1902 ; D. R.-P. 156440 ; 157325 ; Eng. P. 27372 of 1903 ; D. R.-P 160536, 162009 ; Eng. P 4997 ; 21638 of 1904 ; Hochst, D. P. Anm. F. 16863 ; Eng P. 23993 of 1902), also diazotised 1-chloro-*β*-naphthylaminesulphonic acids (Badische, D. R.-P 145906 ; 148882), and 2 : 4-dichloro-*α*-naphthylaminesulphonic acid (Badische, D R.-P. 153298 ; Eng. P. 16995 of 1903), furnish anhydrides (*diazo-oxides*) of hydroxydiazonaphthalenesulphonic acids, *e.g.* for *β*- compounds .



With regard to the second exception, it is known that in the presence of free mineral acid, 1 : 2- and 2 : 1-aminonaphtholsulphonic acids are not diazotised by nitrous acid (Witt, Ber. 1888, 21, 3475), but oxidised to [*β*-]naphthaquinonesulphonic acids (Boniger, Ber. 1894, 27, 24 ; *cf.* Badische, D. R.-P 153298 ; Eng. P. 16995 of 1903). When diazotisation is carried out in the absence of acids other than acetic, oxalic, or tartaric (the nitrous acid required arising from the interaction of the dissolved aminonaphthol hydrochloride or -sulphonic acid with nitrite) and with ordinary dilution, *diazo-oxides* are formed (Weiler-ter-Meer, D. R.-P. 155083).[2] The yield, however, is not good, but becomes almost quantitative in the presence of cupric or ferric salts (Geigy, D. R.-P. 171024 ; Eng. P. 10235 of 1904 ; D. R -P. 172446), zinc salts (Kalle, D. R.-P. 175593 ; 195228 ; Eng. P. 23034 of 1905), nickel salts (Kalle, D. R.-P. 178621), manganese, cobalt or magnesium salts (Kalle, D. R -P. 195322), or mercuric salts (Kalle, D. R.-P. 178936). But as these salts are found to spoil the brightness and solubility of the derived azo- dyes, they may with advantage be replaced by salts of the alkali or alkaline earth metals (Badische, D. R.-P. 189179 ; Eng. P. 10323 of 1906).

The diazo- oxides form non-explosive, yellow, crystalline powders (Geigy, D. R.-P. 171024 ; Eng. P. 10235 of 1904) ; they can be chlorinated (Kalle, D. R. P. 246573 ; 246574 ; Eng. P. 20072 ; 20073 of 1911) ; brominated (Sandoz, D. R.-P. 236656 ; Eng. P. 3508 of 1911) ; nitrated by nitrosulphuric acid without decomposition (Geigy, D. R.-P. 164655 ; Eng. P. 15418 of 1904 ; Kalle, D. R.-P. 176619 ; Bindsch., D. R.-P. 206698) ; and sulphonated by anhydrosulphuric acid (Kalle, D. R.-P. 176618 ; 176620). Probably as the result of their structure, their capacity for coupling



(RH being the amine or phenol with which coupling has taken place) is not pronounced, except for resorcinol (Badische, D. R.-P. 148881) ; the derived hydroxyazo- dyes give fast bluish-black shades on chromed wool (*v.* p. 488).

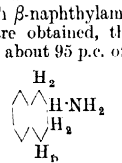
TETRAHYDRONAPHTHALENE DERIVATIVES.

On reduction in boiling amyl alcohol solution with sodium, the naphthylamines and naphthols are converted into tetrahydro- derivatives, of which two types exist :—

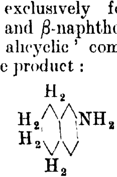
(1) Those termed *alicyclic* (or *ac.*-) derivatives, in which both the substituent and the four added hydrogen atoms are in the same ring.

(2) Those termed *aromatic* (or *ar.*-) derivatives, in which the substituent is in one and the four added hydrogen atoms are in the other ring.

With *α*-naphthylamine and *α*-naphthol, 'aromatic' derivatives are exclusively formed, but with *β*-naphthylamine and *β*-naphthol both types are obtained, the 'alicyclic' compound forming about 95 p.c. of the product :



(*ac.*-derivative.)



(*ar.*-derivative.)

The specific properties which distinguish corresponding derivatives of naphthalene and benzene are suppressed in the tetrahydronaphthalene derivatives, and, in connexion with the naphthalene theory, it may be noted that 'alicyclic' compounds display the characters of the secondary amines and alcohols of the aliphatic series, whereas 'aromatic' compounds show a close analogy in properties with the *o*-xylidines and *o*-xylenols of the benzene series (Bamberger, Annalen, 1890, 257, 1). For a detailed account of tetrahydronaphthalene and its derivatives the article TETRALIN should be consulted.

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[1] As another illustration of the essential difference between the contiguous homonucleal *αβ*- and *ββ*-positions (*cf.* p 417), it may be noted that the diazotisation of 2-amino-3-naphthol-6-sulphonic acid presents no difficulty, the normal type of diazo- compound being formed (Hochst, D. R -P 53076 ; Eng P 15176 of 1889 ; Cassella, D. R.-P. 109932 ; Eng. P. 28107 of 1897).

[2] This difficulty has also been overcome without the formation of diazo-oxides :—

(i.) by esterifying the hydroxyl radicle by means either of acetic anhydride (Gesellsch. D. R.-P 181714 ; Eng. P. 82 of 1905), or of toluene-*p*-sulphonyl chloride (Aktienges., D. R.-P. 193099 ; 196923), diazotisation then proceeding normally ;

(ii.) by using a suspension of the aminonaphtholsulphonic acid in about 4 times its weight of 20 p c. acetic acid, the suspended acid passing into solution as diazotisation proceeds (Kalle, D. R.-P. 188645 ; 190693) ;

(iii.) in the case of di- and tri-sulphonic acids, by carrying out the diazotisation in highly dilute sulphuric acid solution (0·5 mol.) at 0°–5° (Kalle, D. R.-P. 184477).

I. CHLORO-DERIVATIVES.

Introductory.—Naphthalene derivatives, in which chlorine is associated with the carbon atoms of the nucleus, are of two kinds : additive compounds, *e.g.* naphthalene dichloride and tetrachloride, and those in which substitution of chlorine for hydrogen has taken place, *viz.* the chloronaphthalenes.

The formation of chloronaphthalenes can be achieved by the following methods :

(1) From naphthalene or chloronaphthalenes by chlorination (*cf.* Faust and Saame, Annalen, 1871, 160, 65 ; E. Fischer, Ber. 1878, 11, 735 ; Widman, Ber. 1882, 15, 2160 ; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 85 ; Badische, D. R.-P. 234912).

(2) From aminonaphthalenes by diazotisation and the Sandmeyer reaction (*cf.* Friedlander and Szymanski, Ber. 1892, 25, 2081 ; Chattaway and Lewis, Chem. Soc. Trans. 1894, 65, 877).

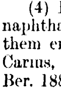
(3) From nitro-, amino-, or hydroxy-naphthalenesulphonic acids by conversion into chloro naphthalenesulphonic acids and subsequent hydrolysis (*cf.* Cleve, Ber. 1892, 25, 2487).

(4) From naphthalenesulphonyl, or chloronaphthalenesulphonyl chlorides, by heating them either with phosphorus pentachloride (*cf.* Carius, Annalen, 1860, 114, 145 ; Armstrong, Ber. 1882, 15, 205), or alone (*cf.* Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 80, 83 ; 1897, 13, 152).

(5) From nitronaphthalene (de Koninck and Marquart, Ber. 1872, 5, 11), and from nitronaphthalenesulphonyl chlorides (Erdmann and Suvern, Annalen, 1893, 275, 232, 252) by distillation with phosphorus pentachloride.

Allusion has been made to the complete series of mono-, di- and tri-chloronaphthalenes and to their use as reference compounds (p. 412). With the exception of α-chloronaphthalene and 1 : 4-dichloronaphthalene which are cheaply produced, these substances are valueless for technical purposes.

As sources of naphthol or naphthylamine derivatives certain of the α-chloronaphthalenesulphonic acids, *viz.* the 4- and 5- mono-, the 4 : 7-di- and the 2 : 4 : 7-tri- sulphonic acids (the last most readily) or 4-chloro- α-nitronaphthalene can be used, as in them the halogen can be exchanged for OH or NH_2 by digestion with caustic alkali or ammonia respectively.



α-**Chloronaphthalene** is obtained when chlorine is passed into boiling naphthalene in the presence of ferric chloride (Oehler, D. P. Anm. O. 1921) until the calculated increase in weight has been attained ; *or* when naphthalene dichloride is decomposed by heat or by alcoholic potash (Faust and Saame, Annalen, 1871, 160, 68 ; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 85) ; *or,* free from other chloro-derivatives, when diazotised α-naphthylamine hydrochloride is warmed with hydrochloric acid (Gasiorowski and Wayss, Ber. 1885, 18, 1940), or cuprous chloride solution. It boils at 263°, and has sp.gr. 1·2025 at 15°.

Reactions.—On sulphonation, it yields *α-chloronaphthalene*-4-, 5-, 6-, and 7-*monosulphonic acids*, the 4 : 7- and a second *disulphonic acid*, and the 2 : 4 : 7-*trisulphonic acid.* Digestion with 20 p.c. caustic soda solution at 300°, or better with 30 p.c methyl alcoholic potash at 210°, converts it into *α-naphthol.* Nitration furnishes mainly 4-*chloro-α-nitronaphthalene.*

Dichloronaphthalenes. A mixture of 1 : 4- and 1 : 5-dichloronaphthalenes is obtained when naphthalene, with a carrier (ferric chloride, iodine, &c.), is chlorinated in carbon tetrachloride solution at −10° to 0° ; the product contains small amounts of the 1 : 2- and 1 : 7-derivatives, which can be removed as sulphonic acids by stirring with sulphuric acid for 20 hours in the cold (Badische, D. R.-P. 234912). The mixture of the 1 : 4- and 1 : 5- isomerides can also be separated by sulphonation with monohydrate (12 pts.) in the cold, as of the two products, sodium 1 : 4-dichloronaphthalene-6-sulphonate is much less soluble in brine than 1 : 5-dichloronaphthalene-3-sulphonate (Badische, D. R.-P. 229912).

1 : 4-Dichloronaphthalene, in 70 p.c. yield and almost pure, is formed by heating naphthalene (6 pts.) with thionyl chloride (13 pts.) during 8 10 hours at 140°–160° (Höchst, D. R.-P. 286489 ; Meyer, Monatsh. 1915, 36, 728). On nitration it yields 5 : 8-*dichloro-α-nitronaphthalene* (Widman, Bull. Soc. chim. 1877, [ii.] 28, 509).

Perchloronaphthalene $C_{10}Cl_8$ is formed by exhaustive chlorination of naphthalene, finally in the presence of antimony trichloride (Berthelot and Jungfleisch, Bull. Soc. chim. 1868, [ii.] 9, 446). It crystallises in long needles, m.p. 203°, is moderately soluble in benzene or light petroleum, and when heated with 70 p.c. anhydro-acid at 50° is converted into a red dyestuff of unknown composition (Badische, D. R.-P. 66611).

Naphthalene tetrachloride $C_{10}H_8Cl_4$ is formed together with oily impurities containing, according to the conditions employed, varying quantities of naphthalene dichloride, α-chloronaphthalene tetrachloride and a dichloronaphthalene tetrachloride, by the action either of chlorine (Faust and Saame, Annalen, 1871, 160, 67) or of potassium chlorate and hydrochloric acid (E. Fischer, Ber. 1878, 11, 735) on naphthalene. According to Leeds and Everhart (J. Amer. Chem. Soc. 1880, 2, 208), the best yield (45 p.c.) is obtained by leaving naphthalene in thin layers in an atmosphere of chlorine until absorption is complete. Extraction of the product with light petroleum, to remove dichloride, and with alcohol, leaves the tetrachloride in a pure state. It crystallises from chloroform in large rhombohedra, m.p. 182°.

Reactions.—On oxidation at 100° with 8·7 times its weight of nitric acid (sp.gr. 1·45), it yields 2 : 3-*dichloro-*[*α-*] *naphthaquinone* (Helbig, Ber. 1895, 28, 505), or, boiled with ten times its weight, *phthalic acid* (Fischer, *l.c.*) ; but with chromic acid at 90° it gives 3 : 4-*dichloro-α-naphthol* (Helbig, *l.c.*). Nitration with fuming acid (sp.gr. 1·5) converts it into a resinous *nitronaphthalene tetrachloride*, from which 5 : 8-*dichloro-α-nitronaphthalene* is readily obtained (Matter, D.R.-P. 317755). Nitronaphthalene dichloride, formed by nitration of naphthalene dichloride, furnishes 8-*chloro-α-nitronaphthalene* (Matter, *l.c.*).

α-Chloronaphthalenesulphonic Acids.

Introductory.—α-Chloronaphthalenesulphonic acids can be obtained by three methods :

(1) From the corresponding α-naphthylaminesulphonic acids (*q.v.*) by diazotisation and interaction with cuprous chloride solution. This affords the easiest way of making the chloronaphthalenesulphonic acids described in this section, which comprise only such products as are obtainable by one or both of the following processes.

(2) From α-chloronaphthalene by sulphonation, the products with sulphuric acid being successively the 4-, the 5-, and a mixture of the 6- and 7-monosulphonic acids as the temperature is raised gradually to 160°-170°, and the 4 : 7- (possibly also the 2 : 7-) disulphonic acid at 180°-190°.

(3) From sodium naphthalene-α- or β-sulphonate by chlorination.

When prepared by the last two methods, these acids can be used for the production of α-naphthylaminesulphonic acids, but the process has no technical importance.

(i.) α-**Chloronaphthalene-4-sulphonic acid** is the chief product when α-chloronaphthalene is sulphonated with chlorosulphonic acid in the cold (Armstrong and Wynne, Chem. Soc Proc. 1890, 6, 86).

Identification.—The *barium* salt, BaA_2+2H_2O, forms sparingly soluble hexagonal plates, and the *potassium* salt, KA, rhombic prisms. The *chloride*, triclinic prisms, m.p. 95° (*amide*, m.p. 187° ; *cf.* Cleve, Ber. 1887, 20, 73) is convertible into 1 : 4-*dichloronaphthalene.*

Reactions.—Digestion with 25 p.c. caustic soda solution at 220° converts it into α-*naphthol-4-sulphonic acid*, and with 25 p.c. ammonia solution at 200° into α-*naphthylamine-4-sulphonic acid.*

(ii.) α-**Chloronaphthalene-5-sulphonic acid**, formed in small quantity when α-chloronaphthalene is sulphonated with chlorosulphonic acid in the cold, becomes the chief product when the sulphonation mixture is heated at 150° (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 87). It can be obtained by chlorinating sodium naphthalene-α-sulphonate with a mixture of sodium chlorate and hydrochloric acid (Rudolph, D. R.-P. 103983 ; Eng. P. 19088 of 1898).

Identification.—The *barium* salt, BaA_2+H_2O, is a sparingly soluble, microcrystalline powder ; the *potassium* salt, KA, forms needles, and the *sodium* salt, NaA, scales. The *chloride*, large prisms, m.p. 95° (*amide*, m.p. 226° ; *cf.* Cleve, *l.c.*) is convertible into 1 : 5-*dichloronaphthalene.*

Reactions.—Digestion with 8 p.c. caustic soda solution at 250° converts it into α-*naphthol-5-sulphonic acid,* and with 25 p.c. ammonia solution at 210° into α-*naphthylamine-5-sulphonic acid.*

(iii.) α-**Chloronaphthalene-6-sulphonic acid**, mixed with the 7-sulphonic acid, is formed when α-chloronaphthalene is heated with 1–1·5 times its weight of sulphuric acid at 160°–170° for many hours (Oehler, D. R.-P. 76396) ; or when a solution of sodium naphthalene-β-sulphonate is chlorinated by means of chlorine or of sodium chlorate and hydrochloric acid (Rudolph, D. R.-P. 101349 ; Eng. P. 19088 of 1898). By fractional crystallisation its calcium, barium, or sodium salt can be separated from the more soluble salt of the 7-sulphonic acid.

Identification.—The *barium* salt, BaA_2+H_2O, a crystalline powder and the *potassium* salt, KA, thin scales, dissolve only sparingly in cold water. The *chloride*, scales, m.p. 114°–115° (*amide*, m.p. 216° ; *cf.* Cleve, *l.c.*) is convertible into 1 : 6-*dichloronaphthalene*

(iv.) α-**Chloronaphthalene-7-sulphonic acid** (*v.* 6-sulphonic acid) gives an easily soluble *barium* salt, BaA_2+3H_2O, scales, and *potassium* salt, $KA+H_2O$, needles. Its *chloride*, large crystals, m.p. 94° (*amide*, m.p. 181° ; *cf.* Cleve, Ber. 1892, 25, 2480) is convertible into 1 : 7-*dichloronaphthalene.*

(v.) α-**Chloronaphthalene-4 : 6-disulphonic acid** is formed when sodium α-chloronaphthalene-6-sulphonate is heated with 10 p c. anhydro-acid at 110° (Rudolph, D. R -P. 104902). Its *chloride*, small needles, m.p. 126°–127°, is convertible into 1 : 4 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

Reaction.—Digestion with caustic soda solution at 230° converts it into 1 : 6-*dihydroxynaphthalene-4-sulphonic acid.*

(vi.) α-**Chloronaphthalene-4 : 7-disulphonic acid** is obtained when α-chloronaphthalene is sulphonated with 45 p.c. anhydro-acid at 20°, or with sulphuric acid at 180°[1] (Oehler, D. R.-P. 74744) ; *or* when sodium α-chloronaphthalene-4-sulphonate is sulphonated with 20 p.c. anhydro-acid at 20° (Oehler, *l.c.*), or at 100° (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 18). The *chloride*, prisms, m.p. 107°, is convertible into 1 : 4 : 6-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reaction.—Digestion with 30 p.c. caustic soda solution at 200°–210° converts it into α-*naphthol*-4 : 7-*disulphonic acid.*

(vii.) α-**Chloronaphthalene-2 : 4 : 7-trisulphonic acid** is the chief product of the sulphonation of α-chloronaphthalene with 45 p.c. anhydro-acid at 80°, *or* of sodium α chloronaphthalene-4-sulphonate with 20 p c. anhydro-acid at 170° (Oehler, D. R.-P. 76230).

Identification.—Its *sodium* salt Na_3A+4H_2O forms small needles (Oehler, *l.c.*), and its *chloride* scales, m p. 215° (Armstrong and Wynne, Chem. Soc. Proc 1890, 6, 126).

Reaction.—Digestion with 12 p.c. caustic soda, solution at 150° converts it into α-*naphthol*-2 : 4 : 7-*trisulphonic acid.*

II. Naphthalenesulphonic Acids.

Introductory.—Naphthalenesulphonic acids can be obtained by the following methods :

(1) Action of sulphuric acid on naphthalene or on naphthalenesulphonic acids.

(2) Elimination of the NH_2 radicle from naphthylaminesulphonic acids (*cf.* the 1 : 3-disulphonic acid).

(3) Exchange of the amino-group of naphthylaminesulphonic acids for the SH or SO_2H radicle, and oxidation of the resulting mercaptan or sulphinic acid (*cf.* the 1 : 2-disulphonic acid).

Of these methods the first is of technical importance and by it ten naphthalenesulphonic acids (two mono-, four di-, three tri-, and one tetra-) have been obtained. As sulphonating agent[1] sulphuric acid, monohydrate or anhydro-acid (oleum) is almost invariably employed. Chlorosulphonic acid is sometimes convenient on the laboratory scale, but for technical purposes its use, or the use of anhydro-acid to which common salt has been added, is disadvantageous (as is also the salting out of a product by the addition of common salt to a sulphonation melt), owing to the destructive effect of hydrochloric acid, the by-product, on the metal of the containing vessel, or the press cloths of the filter press.

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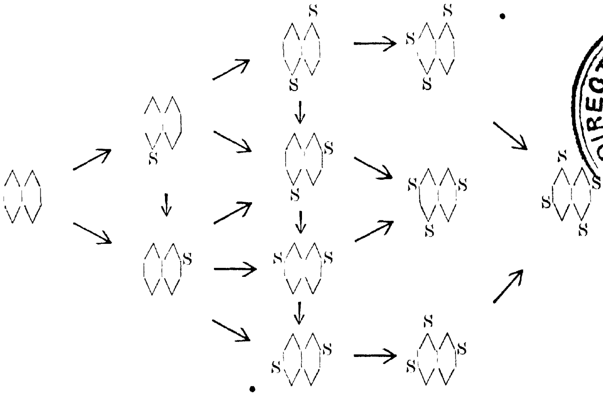
[1] A second acid, possibly the 2 : 7-isomeride yielding an *α-naphtholdisulphonic acid* when digested with 30 p.c. caustic soda solution at 200°, is also formed under these conditions, but no details are given by which it can be identified (Oehler, *l.c.*).

Attention has been called to the fact that sulphuric acid, unlike other substituting agents, gives rise to β-derivatives in amounts depending on the temperature and duration of the reaction as well as on the quantity and concentration of the acid (*v.* p. 413). If the conditions leading to the production of naphthalene-β-sulphonic acid or of naphthalene-2 : 6- or 2 : 7-disulphonic acid, for example, are considered, they show that of the four factors named the concentration and temperature of the acid exercise a preponderating influence in determining the relative positions which the SO_3H radicles will have assumed at the end of a sulphonation.

The following table indicates the constitution of the acids obtained from naphthalene or from naphthalenesulphonic acids by sulphonation; it also shows, by the use of vertical arrowheads, the change in constitution which accompanies a rise in temperature of the reaction from 0° to about 170°. The restriction of the number of naphthalenesulphonic acids obtained by sulphonation to ten seems to be connected with the fact that in no case has a product been isolated from the sulphonation melt containing two sulphonic groups in positions relatively 1 : 2- (*ortho-*), 1 : 4- (*para-*) or 1 : 8- (*peri-*) to one another. Later investigation may account for the existence of this limiting factor; it cannot be due to instability of these configurations except under conditions obtaining in the sulphonation melt, as naphthalene-di-, tri- and tetra-sulphonic acids, in which sulphonic groups occupy respectively these relative positions, have been prepared by the third general method from naphthylaminesulphonic acids and are well-defined compounds.



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The naphthalenesulphonic acids are strong acids; they decompose common salt, and those which contain two or more sulphonic groups furnish by this decomposition acid salts. Like their alkali salts they are easily soluble in water, but the lead, barium, and calcium salts differ much in solubility, and in some cases afford a means of separating the constituents of a sulphonation melt. From the alkali salts, crystalline chlorides, amides, and anilides with definite melting-points, which serve to characterise the acids, can be prepared, and from the chlorides by distillation with phosphorus pentachloride chloronaphthalenes which serve to fix their constitution.

For the purpose of determining the constituents of a sulphonation melt the sparingly soluble α- and β-naphthylamine salts of naphthalene-1 : 5-, 1 : 6-, 2 : 6- and 2 : 7-disulphonic acids have been proposed, as certain of them differ sufficiently in solubility in water or in acetone to admit of qualitative recognition (Ambler, J. Ind. Eng. Chem. 1920, 20, 1081, 1194; Ambler and Wherry, *ibid.* 1086).

The industrial value of the naphthalenesulphonic acids arises from the readiness with which they undergo change in directions such as the following: the loss of sulphonic groups, the exchange of these groups for radicles such as hydroxyl or cyanogen and the formation of substitution derivatives such as chloro- or nitro-naphthalenesulphonic acids.

Elimination of sulphonic groups may be achieved either by hydrolysis with phosphoric or sulphuric acid and superheated steam, or with diluted acid under pressure, or by the aid of sodium amalgam in the cold. In general, sulphonic groups in α-positions are more easily eliminated than those in β-positions (Friedlander and Lucht. Ber. 1893, 26, 3028).

Exchange of sulphonic groups for hydroxyl radicles is effected by fusion of the alkali salt with caustic alkali, or by digestion with caustic alkali solution under pressure. The reaction takes place more readily with α- than with β-

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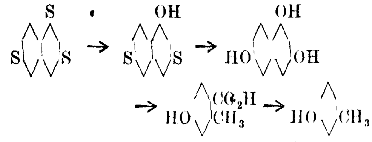
[1] In this article, '**sulphuric acid**,' when not otherwise distinguished, is ordinary concentrated (about 98 p.c.) sulphuric acid of sp gr. 1·845; '**monohydrate**' is 100 p.c. sulphuric acid; and '**anhydro-acid**' is fuming sulphuric acid or '**oleum**' containing dissolved sulphur trioxide, the proportion of which is given when known.

sulphonic groups. Should the naphtholsulphonic acid produced contain a sulphonic group in the 3-position relatively to the hydroxyl, further change may occur, and hydroxytoluic acids or *m*-cresols (from *m*-hydroxytoluic acids) be formed:



With tetrazodiphenyl or diazotised *p*-nitraniline, naphthalene-mono- and di-sulphonic acids form salts of only a moderate degree of stability.[1] In marked contrast with them is the acid salt,

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_3{\cdot}C_{10}H_7+NaSO_3{\cdot}C_{10}H_7+H_2O$$

obtained from naphthalene-*β*-sulphonic acid and diazotised *p*-nitraniline, which is non-explosive, can be transported in the dry state, and under the name Paranil A is largely used as a developer in para-red dyeing (Witt, D. R.-P. 264268; Eng. P. 11290 of 1913).

For technical purposes the acids are valuable as sources of the naphthols, of several naphtholsulphonic acids and of several nitronaphthalenesulphonic acids, these nitro-acids furnishing by reduction naphthylaminesulphonic acids isomeric with those obtained from the naphthylamines by sulphonation.

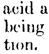
The action of sulphuric acid on naphthalene leads also to the formation of small quantities of two dinaphthylsulphones—the *αβ′*- melting at 123°, and the *ββ′*- at 177° (Stenhouse and Groves, Ber. 1876, 9, 682; Hofmann, Ber. 1884, 17, 1921; Krafft, Ber. 1890, 23, 2364)

Synthetic tanning materials (*e.g.* Neradol N.D.) are obtained either by condensing formaldehyde with the mixed acids formed by the monosulphonation of naphthalene at 130°-140° or by heating the condensation product of naphthalene and formaldehyde (*cf.* Badische, D. R.-P. 207743; Eng. P. 6831 of 1909) with sulphuric acid at 80° until soluble (Badische, D. R.-P. 290965, 290966, 292531).

NAPHTHALENEMONOSULPHONIC ACIDS.

Introductory.—According to the conditions employed, naphthalene on sulphonation with about its own weight of sulphuric acid yields a product containing varying proportions of *α*- and *β*-monosulphonic acids and a small quantity of at least one disulphonic acid. Merz and Weith state that a mixture of naphthalene and sulphuric acid in the proportion of 10 : 9 gave a product containing 80 p.c. of *α*-acid and 20 p.c. of *β*-acid when heated for 3 hours at 100°, but only 25 p.c. of *α*-acid with 75 p.c. of *β*-acid when heated for a further 4 hours at 170°, 15 p.c. of the naphthalene being recovered in the first case and 25 p.c. in the second. Also, that a mixture in the proportion 5 : 4 heated for 8 hours at 160° gave 80 p.c. of *β*-acid, 30 p.c. of the naphthalene employed being recovered (Ber 1870, 3, 195). At temperatures below the melting-point of naphthalene the monosulphonation product is said to be solely the *α*-acid, whether obtained by the use of sulphuric acid at 40°, or of anhydro-acid in the cold (Landshoff, D. R.-P. 50411) or of chlorosulphonic acid added to a solution of the hydrocarbon in carbon disulphide (Armstrong and Wynne, Chem. Soc. Proc. 1886, 2, 231). In the light of Euwes' results (*v.* p. 413) these low-temperature products doubtless contained *β*-acid, but in quantity relatively so small as to escape recognition by the methods of detection then available.

More recently, the question of monosulphonation has been re-examined, but the results, although of much interest, do not affect substantially the conclusion just indicated. Fierz and Weissenbach show that when naphthalene is sulphonated at 0° with twice its weight of sulphuric acid, *β*-acid is formed to the extent of at least 2 p.c. (Helv. Chim. Acta, 1920, 3, 314), and Witt, whose paper includes an historical review of the subject, confirms Euwes' statement of the composition of the product at 161° (*l.c.*) by finding that at 165° the two acids are present in the melt in the ratio of 85 pts. of *β*-acid to 15 pts. of *α*-acid (Ber. 1915, 48, 754).



(i.) **Naphthalene-*α*-sulphonic acid** (*sulphonaphthalic acid*) $C_{10}H_7{\cdot}SO_3H$ is obtained by stirring finely powdered naphthalene with 1·5–2 times its weight of sulphuric acid at 40°–50° until dissolved, the temperature being raised to 70° towards the end of the operation. Care must be taken that the vessel is free from crystals of the *α*-sulphonic acid from a previous operation, otherwise the mixture may solidify before sulphonation is complete. The product, poured into a large bulk of water and separated in the cold from unattacked naphthalene, is neutralised with lime and converted into sodium salt (Landshoff, *l.c.*). Or the sodium salt may be separated by adding common salt to the melt diluted with only a small volume of water.

If the pure acid is required, sulphonation may be carried out at 0° with monohydrate (2 pts.), and the separation obtained by adding a crystal of the *α*-acid to the melt may be freed from unchanged naphthalene by dissolution in water. From the filtrate, concentrated at 35° under, 20 mm. to a density of 1·29–1·3, the *α*-acid separates as a crystalline mass, which can be further purified by fractional precipitation from a highly concentrated solution by hydrogen chloride (Fierz and Weissenbach, *l c.*).

Identification.—The *acid*, $HA+2H_2O$, forms small, easily soluble, non-deliquescent crystals, m.p. 90°, which cannot be dehydrated without decomposition; the salts dissolve easily in water and crystallise in scales.

Composition of salt (Merz, Zeit Chem. 1868, [ii] 4, 394.)	1 part of the salt dissolves in	
	parts of water at 10°	parts of 85p.c. alcohol at 10°.
Potassium salt $+\frac{1}{2}H_2O$	13 (at 11°)	108 (at 11°)
Calcium ,, $+2H_2O$	16·5	19·5
Barium ,, $+H_2O$	87	350
Lead [2] ,, $+3H_2O$	27	11

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[1] *Cf.* Becker, D. R.-P. 81039, 86367, 89998; Fab. prod. Chim. de Thann, D. R.-P. 92237, 94280; Badische, D. R.-P. 263431; Eng. P. 2037 of 1912.

[2] Compare, however, Euwes (Rec. trav. chim. 1909, 28, 303, 304), who assigns $2H_2O$ to the *α*-salt and to the *β*-salt a solubility in water only about one-half that given by Merz.

The *ammonium* salt, NH_4A, and the *zinc*, *cobalt*, *nickel*, *copper* and *cadmium* salts, each with $6H_2O$, have also been described (Fierz and Weissenbach, *l.c.*). The *chloride* forms scales, m.p. 67° (Erdmann, Annalen, 1893, 275, 235), and the *amide* minute crystals, m.p. 150° (Maikopar, Zeit. Chem. 1869, [ii.] 5, 711).

Reactions.—By sulphonation with anhydro-acid in the cold, a mixture of the 1 : 5- and 1 : 6-*disulphonic acids* is obtained. Fusion with caustic alkali converts it into *a-naphthol* Nitration furnishes mainly *a-nitronaphthalene-*8-*sulphonic acid.*

(ii.) **Naphthalene-β-sulphonic acid** is obtained by adding sulphuric acid gradually to an equal weight of naphthalene heated at 160°, the mixture being stirred at this temperature during 3 hours, then at 170° during an hour, and finally at 180° for another hour. The product is converted into sodium salt either by neutralisation with lime after dilution, followed by treatment of the filtrate with sodium carbonate, or by salting out with common salt or sodium sulphate, or (*cf.* Uhlmann, D. R.-P. 229537) crude sodium sulphite. The sodium salt of the α-acid, being the more soluble, remains in the mother liquor. Other ways of separating the β-acid or its sodium salt have been proposed by Boulton (Eng. P. 4459 of 1894), Dennis, who suggests extraction of the β-acid from the melt by means of toluene (Brit. P. 109709), and Southcombe and Downie (Brit. P. 120405).

To obtain the pure acid, 250 grams of naphthalene are kept at 160° while 400 grams of 93·7 p.c. sulphuric acid are stirred in during 15 minutes. Five minutes later the melt is poured into 300 c.c. of water, and from this solution the β-acid (mixed with about 1 p.c. of sulphone) separates in the cold as a crystalline mass, being salted out by the α-acid present. This β-acid, purified by dissolving 600 grams in 300 c.c. of water at 70°, and adding 100 c.c. of hydrochloric acid (d. 1·19), separates as the trihydrate in lustrous scales (Witt, Ber. 1915, 48, 755).

Identification.—The *acid*, $HA+3H_2O$, forms non-deliquescent scales, m.p. 83°, from which the monohydrate, m.p. 124°, and the anhydrous substance, m.p. 91°, which is soluble in toluene, can be obtained (Witt, *l.c.*). The salts crystallise in small scales, and, except those of the alkali metals, are only sparingly soluble in cold water.

Composition of salt (Merz, *l c* ; *cf.* Witt, *l c.*)	1 part of the salt dissolved in	
	parts of water at 10°	parts of 85 p c. alcohol at 10°.
Potassium salt$+\frac{1}{2}H_2O$	15	115
Calcium „ anhydrous . . .	76	437
Barium „ $+H_2O$	290	1950
Lead „ $+H_2O$	115[1]	305

The *sodium* salt, NaA, dissolves in 16·5 parts of water at 23·9° (E. Fischer, Ber. 1906, 39, 4144)[2]; the *ammonium* salt, NH_4A, and the *zinc*, *cobalt*, *nickel*, *copper* and *cadmium* salts, each with $6H_2O$, have also been described (Witt, *l.c.*). The ferrous salt FeA_2+6H_2O forms large glistening plates, sparingly soluble in cold, readily in hot water (Ambler, J. Ind. Eng. Chem. 1920, 12, 1083). The *chloride* forms scales, m p. 78° (E. Fischer and Bergell, Ber. 1902, 35, 3780) and the *amide* sparingly soluble scales, m p. 213° (Cleve, Bull. Soc chim. 1876, [ii.] 25, 258).

Reactions.—On sulphonation, it yields initially the 1 : 6- and at 160°–170° a mixture of the 2 : 6- and 2 : 7-*disulphonic acids.* Fusion with caustic alkali converts it into *β-naphthol.* Nitration furnishes a mixture of *a-nitronaphthalene*-6- and 7-*sulphonic acids* in equal amount.

Naphthalenedisulphonic Acids.

Introductory.—The four naphthalenedisulphonic acids obtained by sulphonation are the 1 : 5-, 1 : 6-, 2 : 6-, and 2 : 7- isomerides, and are all heteronucleal. The order in which these acids make their appearance in the sulphonation melt as the temperature rises is clear so far as the 1 : 5- and 1 . 6- compounds are concerned, the former being first, but there is less agreement whether the 2 : 7- precedes the 2 : 6- isomeride although the balance of evidence seems to favour this view.

(i.) **Naphthalene-1 : 2-disulphonic acid** is formed from α-naphthylamine-2-sulphonic acid by conversion either into the thionaphtholsulphonic acid (Bayer, D. R.-P. 70296 ; Eng P. 11465 of 1892 ; Armstrong and Wynne, Chem. Soc. Proc. 1893, 9, 168) or into the sulphinic acid (Gattermann, Ber. 1899, 32, 1156), and oxidation of these compounds by potassium permanganate in alkaline solution.

Identification.—The *potassium* salt ($+\frac{2}{3}H_2O$) forms very soluble flat prisms, and yields not a chloride but an *anhydride* (prisms, m.p. 198°) by interaction with phosphorus pentachloride (Armstrong and Wynne, *l.c.*).

(ii.) **Naphthalene-1 : 3-disulphonic acid** is obtained from β-naphthylamine-6 : 8-disulphonic acid or β-naphthylamine-5 : 7-disulphonic acid by boiling the corresponding hydrazine with copper sulphate solution (Armstrong and Wynne, Chem. Soc. Proc 1890, 6, 13, 129), *or* from α-naphthylamine-2 : 4-disulphonic acid by boiling its diazo- compound with alcohol (Höchst, D. R.-P. 92082).

Identification.—The *barium* salt, $BaA+4H_2O$, *potassium* salt, K_2A+2H_2O, and the *sodium* salt are crystalline and very soluble in water. The *chloride* forms easily soluble prisms, m.p. 137°, convertible into 1 : 3-*dichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—Fusion with caustic soda converts it into *a-naphthol-3-sulphonic acid*, but digestion with 60 p.c. caustic soda solution at 250°–300° gives *o-toluic acid* (Kalle, D. R.-P. 79028 ; *cf.* Friedländer and Rüdt, Ber. 1896, 29, 1611).

(iii.) **Naphthalene-1 : 4-disulphonic acid** is obtained from α-naphthylamine-4-sulphonic acid as described under the 1 : 2- acid (*cf.* also Bayer, D. R.-P. 95830 ; Eng P. 26139 of 1896).

Identification.—The *potassium*, $K_2A+1\frac{1}{2}H_2O$, and *sodium* salts are crystalline and easily soluble. The *chloride* forms four-sided plates, m.p. 160°

[1] See footnote [2] on p. 422.

[2] According to Cooke, the solubility of the sodium salt in water is: at 25°, 5·58 g.; 30°, 6·24 g.; 40°, 7·98 g.; 50°, 9·75 g.; 65°, 14·6 g. in 100 g. of solution, but if sodium chloride or sulphate be present in solution to the extent of about 10 g. in 100 g. it is reduced practically to zero (J. Soc. Chem. Ind. 1921, 40, 56T, 239T).

(Armstrong and Wynne, Chem. Soc. Proc. 1893, 9, 168).

Reaction.—By nitration it is converted into *a-nitronaphthalene*-5 : 8-*disulphonic acid.*

(iv.) **Naphthalene-1 : 5-disulphonic acid** (so-called *Armstrong's acid*; *naphthalene*-[γ-]*disulphonic acid* of Armstrong and Wynne; *naphthalene*-[δ-]*disulphonic acid* of Beilstein, Schultz, &c.) is formed together with the 1 : 6-disulphonic acid when 23 p.c. anhydro-acid is added gradually to one-fifth its weight of naphthalene in the cold (Aktienges., D. R.-P. 45776; Eng. P. 4625 of 1888). If four times the weight of 30 p.c. anhydro-acid be used, and the product poured into 3–4 parts of water, a quantitative separation of the 1 : 5-disulphonic acid is obtained. Or, as acid sodium salt, the 1 : 5-disulphonic acid can be separated from the 1 : 6-isomeride by adding common salt to the sulphonation product (Ewer and Pick, D. P. Anm. E. 2619). It is also obtained by the action of sulphuric anhydride or of chlorosulphonic acid in calculated quantity on naphthalene (Armstrong and Wynne, Chem. Soc. Proc. 1886, 2, 231; 1887, 3, 42)

Preparation.—Dry sodium naphthalene-*a*-monosulphonate is stirred into twice its weight of anhydro-acid at 20°, and the mixture afterwards heated for an hour at 60°–70°. To the product, diluted with ten times its weight of water, an equal volume of hot brine is added, and the acid sodium salt, which separates as the solution cools, is purified by recrystallisation (Schultz, Chemie d. Steinkohlenth., 3rd ed., 1, 189; *cf.* Friedlander and Kielbasinski, Ber. 1896, 29, 2574).

Identification.—The *acid* crystallises in very soluble lustrous, white, non-hygroscopic scales. The *lead* salt, $PbA+3H_2O$, *barium* salt, $BaA+4H_2O$, and *calcium* salt, $CaA+3H_2O$, are easily soluble in water, but when dehydrated dissolve only very slowly in it. The *potassium* salt, K_2A+2H_2O, in scales, dissolves in 8·04 parts of water at 12°; the *sodium* salt ($+2H_2O$), in scales, dissolves in 7·99 parts of water at 19° (Ewer and Pick, D. R.-P. 41934). The *chloride* forms needles or small prisms, m.p. 183°, convertible into 1 : 5-*dichloronaphthalene* (Armstrong, Ber. 1882, 15, 205).

Reactions.—On sulphonation, it yields the 1 : 3 : 5-*trisulphonic acid.* Fusion with caustic soda converts it into *a-naphthol*-5-*sulphonic acid* and 1 : 5-*dihydroxynaphthalene.* Nitration furnishes both *a-nitro-* and *β-nitro-naphthalene*-4 : 8-*disulphonic acid* and eventually 1 : 6-*dinitronaphthalene*-4 : 8-*disulphonic acid.*

(v.) **Naphthalene-1 : 6-disulphonic acid** (*naphthalene*-[γ-]*disulphonic acid* of Beilstein and of Schultz) is formed together with naphthalene-1 : 5-disulphonic acid (*q.v.*) when naphthalene is sulphonated with 23 p.c. anhydro-acid in the cold. It also occurs in the product formed when naphthalene is heated with 5 times its weight of sulphuric acid at 160° for 4 hours (Armstrong, Ber. 1882, 15, 204). Alternatively it is obtained when naphthalene is heated with 5 times its weight of monohydrate at 90°–110°, or with sulphuric acid at 90°, and subsequently with strong anhydro-acid at 110°–120° (Badische, D. P. Anm. B. 9514; *cf.* Bernthsen, Ber. 1889, 22, 3328; Schultz, Ber. 1890, 23, 77).

Preparation.—Dry sodium naphthalene-*β*-sulphonate is sulphonated with twice its weight of 25 p.c. anhydro-acid at the temperature of a water bath, and the product either mixed with half its volume of water, whereby in the cold most of the disulphonate separates as acid sodium salt, or is converted into sodium salt in the usual way. In the latter case, by concentration of the solution to a relatively small bulk, the very soluble sodium salt separates in characteristic needles (Ewer and Pick, D. R.-P. 45229). A pure product is also obtained when an excess of chlorosulphonic acid is employed instead of anhydro-acid in the cold (Armstrong and Wynne, Chem. Soc. Proc 1886, 2, 231; 1889, 5, 10).

Identification.—The *lead* salt, $PbA+3\frac{1}{2}H_2O$, *barium* salt, $BaA+4H_2O$, and *calcium* salt, $CaA+4H_2O$, are readily soluble in water; the *potassium* salt, K_2A+H_2O, dissolves in 3·4 parts and the *sodium* salt, Na_2A+7H_2O, in 3·34 parts of water at 16·5°. The *chloride* forms small prismatic aggregates, m.p. 129°, convertible into 1 . 6-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1886, 2, 232; 1888, 4, 106).

Reactions.—On sulphonation, it yields the 1 : 3 : 6-*trisulphonic acid.* Fusion with caustic soda converts it into 1 . 6-*dihydroxynaphthalene.* Nitration furnishes mainly *a-nitronaphthalene*-3 . 8-*disulphonic acid*, with *β-nitronaphthalene*-4 · 7-*disulphonic acid* as minor product, and eventually 1 : 6-*dinitronaphthalene*-3 . 8-*disulphonic acid.*

(vi.) **Naphthalene-1 : 7-disulphonic acid** can be obtained from *a*-naphthylamine-4 : 6-disulphonic acid by boiling the corresponding hydrazine with copper sulphate solution (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

Identification.—The *potassium* salt ($+H_2O$) is microcrystalline. The *chloride* forms scales, m.p. 122·5°, convertible into 1 : 7-*dichloronaphthalene* (Armstrong and Wynne, *l.c.*).

(vii.) **Naphthalene-1 : 8-disulphonic acid** is formed from *a*-naphthylamine-8-sulphonic acid by oxidation of the corresponding thionaphthol, as described under the 1 : 2-acid (Bayer, *l.c.*; Armstrong and Wynne, *l.c.*).

Identification.—The *potassium* salt ($+H_2O$) forms sparingly soluble four-sided scales, and yields not a chloride, but an *anhydride* (sparingly soluble prisms, m.p. 227°) by interaction with phosphorus pentachloride (Armstrong and Wynne, *l.c.*).

(viii.) **Naphthalene-2 : 6-disulphonic acid** ([*β*-] *naphthalenedisulphonic acid* of Ebert and Merz). For formation and preparation, *v.* naphthalene-2 : 7-disulphonic acid.

Identification.—The *acid* forms small, deliquescent scales, extremely soluble in water. The normal salts (*v.* 2 : 7-acid) contain less water of crystallisation, crystallise less readily, and are less soluble than the corresponding salts of the 2 : 7-acid; the *lead, barium,* and *calcium* salts of the 2 : 6-acid are characterised, moreover, by the slowness with which they again dissolve when once separated from solution. The *chloride* forms small needles, m.p. 226° (Ebert and Merz, Ber. 1876, 9, 598), convertible into 2 : 6-*dichloronaphthalene* (Cleve, Bull. Soc. chim. 1876, [ii.] 26, 244; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 127).

Reactions.—On sulphonation it yields the 1 : 3 : 7-*trisulphonic acid.* Fusion with caustic alkali converts it into *β-naphthol-6-sulphonic acid* and, finally, 2 : 6-*dihydroxynaphthalene*. Nitration furnishes *a-nitro-* and 1 : 5-*dinitro-naphthalene*-3 : 7-*disulphonic acids*.

(ix.) **Naphthalene-2 : 7-disulphonic acid** ([α-] *naphthalenedisulphonic acid*), according to Ebert and Merz, is obtained, together with about an equal amount of the 2 : 6-acid, when a mixture of 1 part of naphthalene and 5 parts of sulphuric acid is heated at 160° for 4 hours; when heated at 180° for 24 hours, however, the same mixture gives a product consisting almost entirely of the 2 : 6-acid. Pure 2 : 7-acid, also, is converted into the 2 : 6-acid by prolonged heating with sulphuric acid at 180° (Ber. 1876, 9, 595). Armstrong, however, found that the product formed by heating the mixture at 180° for 24 hours contains a smaller proportion of the 2 : 6-acid than stated by Ebert and Merz; that a third acid, subsequently recognised as the 1 : 6-disulphonic acid, is present in the 160° melt; and that sulphonation at 140° leads to the formation of a product differing greatly from that obtained at 160°, owing, no doubt, to the presence of an increased proportion of the 1 : 6-acid and almost entire absence of the 2 : 6-isomeride (*cf.* Ber. 1882, 15, 204).

Preparation.—(1) Naphthalene is heated with 5 times its weight of sulphuric acid at 160° for 5 hours, and the product converted into calcium salt in the usual way. The separation of the isomeric disulphonic acids can be based on the very slight solubility in water of the calcium 2 : 6-disulphonate, after it has been dehydrated at 200°–230° (Ebert and Merz, *l.c.*; *cf.* Freund, D. R.-P. 27346; Eng. P. 1069 of 1883). Alternatively, advantage may be taken of the difference in solubility of the calcium salts of the 2 : 6-, 2 : 7-, and 1 : 6 acids in concentrated brine, as the salt of the 2 : 6-acid is practically insoluble in hot and cold, the salt of the 2 : 7-acid moderately soluble in hot but only very sparingly soluble in cold, and the salt of the 1 : 6-acid fairly readily soluble in cold brine (Landshoff, D. R.-P. 48053).

(2) Two methods, in neither of which is reference made to the occurrence of 1 : 6-acid in the sulphonation product, have been described by Baum for the production and separation of the 2 : 6- and 2 : 7-acids (D. R.-P. 61730):—

(*a*) Sodium naphthalene-β-sulphonate (230 kilos.) is stirred into monohydrate (500 kilos.) or sulphuric acid (600 kilos.) kept at 160°–170°, and afterwards heated at 180° for 6–8 hours. The product, after dilution with water and conversion into calcium salt, is concentrated until the solution contains about 30 p.c. of the salt and then allowed to cool. By this means the greater part of the salt of the 2 : 6-acid (52 kilos.) is separated. The filtrate, converted into sodium salt, is evaporated to dryness, and the salt of the 2 : 7-acid (200 kilos.) extracted by twice its weight of warm water, the solution being allowed to cool to 20° before filtration. The residue (80 kilos.) is a mixture of the sodium salts of the 2 : 6- and 2 : 7- acids, which may be worked up with the mixed sodium salt of a subsequent operation.

(*b*) Potassium pyrosulphate (300 kilos.) is dissolved in fused naphthalene-β-sulphonic acid (250 kilos.) at 160°–165°, and the solution mixed with monohydrate (120 kilos.) also heated at 160°–170°. By conversion of the product into potassium salt in the usual way and concentration of the solution to a small bulk, the less soluble salt of the 2 : 6-acid (54–60 kilos.) is separated from the more soluble salt of the 2 : 7-acid (386–390 kilos.), the yield of the latter being much greater than in the first process.

(3) Naphthalene vapour is allowed to ascend a tower heated at 220°–230°, down which sulphuric acid descends over pebbles. The product, being subjected to heat during only a brief period, whereby transformation into isomeric acids is impeded, is said to consist of the 2 : 7-acid mixed with only small amounts of the 2 : 6-acid and some sulphuric acid (Gibbs, Ambler, and the Selden Co., Brit. P. 131970).

Identification.—The *acid* crystallises in long, deliquescent needles, very soluble in water. The salts are more soluble and crystallise better than those of the 2 : 6-acid; the composition of the crystalline salts and the solubility of the anhydrous salts (1 pt.) of both the 2 : 6- and 2 : 7-acids in water at 18° are compared in the table (Ebert and Merz, *l.c.*):—

2 : 7 or [α-]		2 : 6 or [β-]	
$PbA+2H_2O$	easily	$PbA+H_2O$	sparingly
$BaA+2H_2O$	82·2 (19°)	$BaA+H_2O$	"
$CaA+6H_2O$	6·2	CaA	16·2
K_2A+2H_2O	1·4	K_2A	19·2
Na_2A+6H_2O	2·2	Na_2A+H_2O	8·4 (19°)

The *chloride* forms four- or six-sided prisms, m.p. 158° (Ebert and Merz, *l.c.*) convertible into 2 : 7-*dichloronaphthalene* (Cleve, Bull. Soc. chim. 1876, [ii.] 26, 244; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 12).

Reactions.—On sulphonation, it yields the 1 : 3 : 6-*trisulphonic acid*. Fusion with caustic alkali converts it into *β-naphthol-7-sulphonic acid* and 2 : 7-*dihydroxynaphthalene*. Nitration furnishes 1 : 8-*dinitronaphthalene*-3 : 6-*disulphonic acid*.

NAPHTHALENETRISULPHONIC ACIDS.

Introductory.—According to Gurke and Rudolph, a naphthalenetrisulphonic acid is obtained by the sulphonation of naphthalene either with 8 times its weight of 24 p.c. anhydro-acid at 180°, or with 6 times its weight of 40 p.c. anhydro-acid at 80°–100°; also by the sulphonation of naphthalenemono- and di-sulphonic acids and their salts with a proportionately smaller quantity of anhydro-acid (D. R.-P. 38281; Eng. P. 15716 of 1885). Two acids, at least, are obtained by this process, the 1 : 3 : 5-trisulphonic acid, which is the chief product at the lower temperature as Erdmann states (Ber. 1899, 32, 3188), being replaced by the 1 : 3 : 6-trisulphonic acid, the final trisulphonation product at the higher temperature (*cf.* Fierz and Schmid, Helv. Chim. Acta, 1921, 4, 381). As a third acid, the 1 : 3 : 7-derivative, can be obtained by the sulphonation of naphthalene-2 : 6-disulphonic acid, its presence in the mixture, although not recorded, is at least probable.

The naphthalenetrisulphonic acids in which two of the three sulphonic groups are relatively in the *meta-* position yield hydroxytoluic acids by digestion with caustic soda solution at 250° (Kalle, D. R.-P. 91201), and brown dyes, possibly derived from them, by digestion with sodium sulphide, sulphur, and water at 240° (Kalle, D. R -P. 98439).

(i.) **Naphthalene-1 : 3 : 5-trisulphonic acid** is formed when sodium naphthalene-1 : 5-disulphonate (2 pts.) is heated either with monohydrate (3 pts.) during one hour at 50°, 67 p.c. anhydro-acid (2·8 pts.) being then added gradually during a second hour at this temperature, and the mixture afterwards heated at 90° during a further 3 hours, or until disulphonate is no longer precipitated from a sample by brine (Kalle, D. P. Anm K. 11104 ; Eng. P. 1641 of 1894 ; Erdmann, Ber 1899, 32, 3188), or with 20 p c. anhydro-acid (6 pts.) the temperature being gradually raised to 130° and maintained at this point until sulphonation as tested by brine is complete (Fischesser, D. P. Anm. F. 7059 ; Bayer, D. P. Anm. F. 7004 ; Eng. P. 17141c of 1893). It is also formed by oxidising with permanganate the thionaphthol or the sulphinic acid obtained from *β*-naphthylamine-4 : 8-disulphonic acid (Bayer, D. R.-P. 70296 ; Eng. P. 11465 of 1892 ; Gattermann, Ber. 1899, 32, 1158).

Identification.—The *acid* is very soluble in water, and its behaviour recalls that of the strongest non-volatile mineral acids ; the *sodium* salt, Na_3A+4H_2O, forms needles very soluble in water, but only sparingly so in dilute alcohol. The *chloride*, rhombic prisms, m.p 146° (Fischesser, *l.c.* ; Gattermann, *l.c.*) is convertible into 1 : 3 : *5-trichloronaphthalene* (Kalle, *l c* ; D. R.-P. 82563).

Reactions.—On sulphonation it yields *naphthalene*-1 : 3 . 5 : 7-*tetrasulphonic acid.* Fusion with caustic alkali converts it into *α-naphthol*-3 : 5-*disulphonic acid* and 1 : 5-*dihydroxynaphthalene*-3-*sulphonic acid*, but digestion with strong caustic soda solution at 250° gives o-*hydroxy*-o-*toluic acid* (Kalle, D. R.-P. 91201 ; Eng. P. 16559 of 1894). Nitration furnishes *α-nitronaphthalene*-4 : 6 : 8-*trisulphonic acid.*

(ii.) **Naphthalene-1 : 3 : 6-trisulphonic acid** is obtained when sodium naphthalene-1 : 6- or 2 : 7-disulphonate is heated with twice its weight of 24 p.c. anhydro-acid, the temperature being raised gradually to 180° (*cf.* Gurke and Rudolph, D. R.-P. 38281 ; Eng. P. 15716 of 1885 ; Bayer, D. R.-P. 63015), or, mixed with 1 : 3 : 5-trisulphonic acid, when naphthalene or sodium naphthalene-*β*-sulphonate is heated with 40 p.c. anhydro-acid at 150°–160° (Gurke and Rudolph, *l c.*) and when naphthalene is heated with 3·5–4 times its weight of chlorosulphonic acid at 150° for an hour (Armstrong and Wynne, Chem. Soc. Proc. 1887, 3, 146). It is formed also by eliminating the amino-group either from *α*-naphthylamine-2 : 4 : 7-trisulphonic acid (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 125) or from *β*-naphthylamine-3 : 6 : 8-trisulphonic acid (Dressel and Kothe, Ber. 1894, 27, 2154).

Preparation.—Monohydrate (380 pts.) is added very slowly to naphthalene (256 pts.) at 165°, the melt kept at this temperature for an hour, then cooled to 75°, diluted with monohydrate (120 pts.) cooled to 50°, and mixed cautiously with 60 p.c. anhydro-acid (900 pts.), stirring being continuous, and finally heated at 165° for 6 hours to ensure complete conversion of mono- into tri-sulphonic acid, which without being isolated is then available for nitration. The yield of 1 : 3 : 6-trisulphonic acid may amount to 60 p.c. of that calculated (Fierz-David, Dye Chemistry, p. 12).

Identification.—The *sodium* salt Na_3A+5H_2O forms very soluble needles and the *chloride* small prisms, m.p. 194° (Armstrong and Wynne, *l.c.*, Dressel and Kothe, *l c.*).

Reactions.—Heated with 50 p.c. caustic soda solution at 170°–180°, it yields *α-naphthol*-3 : 6-*disulphonic acid*, but with 90 p.c. caustic soda at 250° 1 : 6-*dihydroxynaphthalene*-3-*sulphonic acid.* Nitration converts it into *α-nitronaphthalene*-3 : 6 : 8-*trisulphonic acid.*

(iii.) **Naphthalene-1 : 3 : 7-trisulphonic acid** is obtained when sodium naphthalene-2 : 6-disulphonate (1 pt.) dissolved in monohydrate (3 pts.), is heated with 60 p.c. anhydro-acid (1 pt.) on a water bath until a test, on addition of common salt, gives no separation of the disulphonate (Cassella, D. R.-P. 75432). It is also formed by oxidising with permanganate the thionaphthols from *α*-naphthylamine-3 : 7-disulphonic acid and *β*-naphthylamine 6 : 8-disulphonic acid (Bayer, D. R.-P. 70296 ; Eng. P. 11465 of 1892), and by eliminating the amino-group from *β*-naphthylamine-3 5 : 7-trisulphonic acid (Dressel and Kothe, Ber. 1894, 27, 1203).

Identification.—The *chloride* forms large prisms, m p. 165°–166° (Dressel and Kothe, *l.c.*).

Reactions.—On sulphonation it yields *naphthalene*-1 : 3 · 5 : 7-*tetrasulphonic acid.* Digestion with 50 p.c. caustic soda solution at 260° converts it into p-*hydroxy*-o-*toluic acid* (Kalle, D. R.-P. 91201 ; Eng P. 16559 of 1894). Nitration furnishes *α-nitronaphthalene*-3 : 5 · 7-*trisulphonic acid.*

(iv.) **Naphthalene-1 : 4 : 8-trisulphonic acid** is obtained by oxidising with permanganate the thionaphthol or the sulphinic acid prepared from *α*-naphthylamine-4 : 8-disulphonic acid (Bayer, D. R.-P. 70296 ; Eng P 11465 of 1892 ; Gattermann, Ber. 1899, 32, 1156).

Identification.—The *chloride* forms clusters of needles, m p. 156°–157° (Gattermann, *l.c.*).

(v.) **Naphthalene-2 : 3 : 6-trisulphonic acid,** obtained by oxidising with permanganate the thionaphthol from *β*-naphthylamine-3 : 6-disulphonic acid (Bayer, *l.c.* ; Armstrong and Wynne, Chem. Soc. Proc. 1893, 9, 168), is also the product formed by eliminating the amino-group from *β*-naphthylamine-3 : 6 : 7-trisulphonic acid (Dressel and Kothe, Ber. 1894, 27, 1202).

Identification.—The *potassium* salt ($+5H_2O$) is microcrystalline ; the *chloride* forms flat prisms, m.p. 200° (Armstrong and Wynne, *l.c.*).

The following acids :—

(vi.) **Naphthalene-1 : 2 : 5-trisulphonic acid,**

(vii.) **Naphthalene-1 : 2 : 6-trisulphonic acid,**

(viii.) **Naphthalene-1 : 3 : 8-trisulphonic acid,**

(ix.) **Naphthalene-1 : 4 : 7-trisulphonic acid,**

obtained, like the 2 : 3 : 6-trisulphonic acid, from the corresponding thio-*α*- or *β*-naphtholdisulphonic acids by oxidation, form *sodium* salts which are very soluble in water (Bayer, *l.c.*), but have not been further described.

NAPHTHALENETETRASULPHONIC ACIDS.

Introductory.—Each of the two methods employed for the tetrasulphonation of naphthalene has been stated to furnish more than one tetrasulphonic acid. Senhofer (Monatsh. 1882, 3, 111), by using a mixture of sulphuric acid with phosphoric oxide at 260° for 3–4 hours obtained a product which by fractional crystallisation of the mixed barium or copper salt furnished an acid now identified by Fierz and Schmid as the 1 : 3 : 5 : 7-tetrasulphonic acid (Helv. Chim. Acta, 1921, 4, 381). With 40 p.c. anhydro-acid at 160° for 9 hours, or with chlorosulphonic acid (Bayer, D. R.-P. 40893), at least two tetrasulphonic acids were said to be formed, and to avoid the production of isomerides, the 2 : 6-disulphonic acid replaced naphthalene in later developments of the process (Bayer, D. R.-P. 79054; 80464; Eng. P. 25074 of 1893; *cf.* however, D. R.-P. 89242), furnishing, like the 1 : 3 : 7-trisulphonic acid under similar conditions, a tetrasulphonic acid, the chloride of which melted at 261°-262° (Bayer, D. P. Anm. F. 7224; Eng. P. *l.c.*).

On reinvestigating the subject, Fierz and Schmid (*l.c.*) have reached the following conclusions:—

(i.) That energetic sulphonation with anhydro-acid converts naphthalene into a mixture of the 1 : 3 : 6-trisulphonic and the 1 : 3 : 5 : 7-tetrasulphonic acids;

(ii.) That the 1 : 3 : 5 : 7-derivative is the only tetrasulphonic acid arising from the sulphonation of naphthalene;

(iii.) That this tetrasulphonic acid is formed very readily in the melt, but independently of the 1 : 3 : 6-trisulphonic acid unless by the use of only weakly fuming sulphuric acid isomerisation occurs followed by further sulphonation.[1]

(i.) **Naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid** is obtained when calcium naphthalene-2 : 6-disulphonate, dried at 200°, is heated with 3 times its weight of 25 p.c. anhydro-acid at 90° during 4 hours and then at 260° during 6 hours. The product is converted into sodium salt, which can be separated from a hot concentrated solution by common salt as a heavy sand-like precipitate (Bayer, D. R.-P. 79054; Eng. P. 25074 of 1893).

Identification.—The *barium* salt Ba_2A+14H_2O is efflorescent, that with $8H_2O$ is stable in the air (Fierz and Schmid, Helv. Chim. Acta, 1921, 4, 381). The *chloride* forms very sparingly soluble, compact, cubical crystals, m.p. 261°–262° (Bayer, D. P. Anm. F. 7224; Fierz and Schmid, *l.c.*)

Reactions.—Fusion with caustic alkali converts it into 1 : 3 : 5-*trihydroxynaphthalene*-7-*sulphonic acid*, but digestion with 15 p.c. caustic soda solution furnishes *a-naphthol*-3 : 5 : 7-*trisulphonic acid* and with 60 p.c. solution a mixture of the isomeric 1 : 3-*dihydroxynaphthalene*-5 : 7- and 1 : 5-*dihydroxynaphthalene*-3 : 7-*disulphonic acids*. It cannot be nitrated.

(ii.) **Naphthalene-1 : 3 : 6 : 7-tetrasulphonic acid** has been prepared by oxidising with permanganate the thionaphthol obtained from *β*-naphthylamine-3 : 6 : 8-trisulphonic acid (Bayer, D. R.-P. 70296; Eng. P. 11465 of 1892).

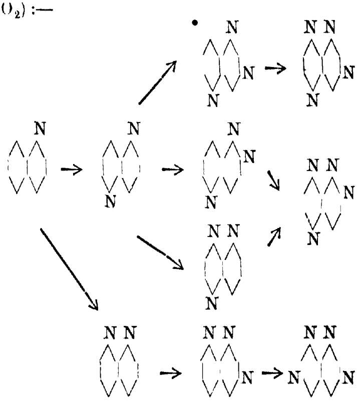
Identification.—The *sodium* salt forms a very soluble granular mass. The *chloride* crystallises in needles, m.p. 309°–310°, sparingly soluble in benzene (Bayer, D. P. Anm. F. 7224).

(iii.) **Naphthalene-1 : 3 : 6 : 8-tetrasulphonic acid** is obtained similarly from *a*-naphthylamine-3 : 6 : 8-trisulphonic acid.

Identification.—The *barium* salt is only sparingly soluble, but the crystalline *sodium* salt easily soluble in water. The *chloride* short prisms, m.p. 282°–283°, dissolves only very sparingly in benzene, but more readily in acetone (Bayer, *l.c.*).

III. NITRO- DERIVATIVES.

Introductory.—The action of nitric acid on naphthalene was first investigated by Laurent (Ann. Chim. Phys. 1835, [ii.] 59, 376; *cf.* Lautemann and Aguiar, Bull. Soc. chim. 1865, [ii.] 3, 261) who described *a*-nitronaphthalene under the name nitronaphthalase. It is now recognised that one mono-[2], two di-, four tri-, and three tetra-[3] nitronaphthalenes can be obtained from naphthalene by nitration under suitable conditions,[4] the relationship between them being shown in the scheme (N is used for NO_2):—



From this scheme it will be seen that, unlike SO_3H radicles in the presence of sulphuric acid, NO_2 radicles in nitration products of nitronaphthalene are found in 1 : 2-(*ortho*-), 1 : 4-(*para*-), and 1 : 8-(*peri*-) positions. Further, as illustrating the difference between nitrobenzene and *a*-nitronaphthalene, it may be pointed out that whereas, by further nitration, the former yields *meta*dinitrobenzene as chief product, the latter gives not the 1 : 3-(*meta*-) dinitronaphthalene but two *heteronuclear aa*-dinitronaphthalenes.

The nitronaphthalenesulphonic acids are described in this section, the nitronaphthylamines and nitronaphthols in connexion with the corresponding naphthylamines and naphthols (*q.v.*).

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[1] Fierz and Schmid further suggest that the simultaneous formation of the tri- and tetra- sulphonic acids accounts to a large extent for the apparent loss of material in the production of H-acid from the trisulphonation melt, in which only the trisulphonic acid can be nitrated.

[2] Possibly accompanied by a very small amount of the isomeric *β*-nitronaphthalene (*q.v.*).

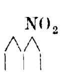
[3] Five, if Dhar's 1 : 2 : 6 : 8- and Aguiar's tetranitronaphthalenes be included (*q.v.*).

[4] The extent to which nitration proceeds with a mixture of nitric and sulphuric acids in molecular proportion depends on the relative proportion of water present: thus with from 0–20/25 p.c. of water, tetra-; 25–50 p.c., tri-; 50–60 p.c., tri- and di-; 60–65 p.c., di-; and in greater amount mono-nitronaphthalene (Saposhnikov, Chem. Soc. Abstr. 1915, 108, i, 393).

By reduction, usually with iron and dilute sulphuric acid, the nitronaphthalenesulphonic acids are converted into the corresponding naphthylaminesulphonic acids, which in not a few cases are of technical importance, being isomeric with those obtained from the naphthylamines by sulphonation.

Unlike nitrated hydrocarbons of the benzene series, the nitronaphthalenes are of little importance as explosives. Crude tetranitronaphthalene, for example, obtained by heating crude dinitronaphthalene with 15 times its weight of a mixture containing 30 p.c. of nitric acid (sp gr. 1·5) and 70 p.c. of sulphuric acid at a temperature not exceeding 130° for an hour, is almost insensitive to detonation and percussion, and when heated burns quietly with a smoky flame without explosion (Escales, Nitrosprengstoffe, ed. 1915, 168, 331).

NITRONAPHTHALENES.



(i.) α-**Nitronaphthalene**, for laboratory purposes, may be prepared by adding very finely powdered naphthalene (128 gr.) to a mixture of 60 p.c. nitric acid (103 gr.) and 80 p.c. sulphuric acid (300 gr.), stirring continuously for 6 hours at 50°, and completing the reaction at 60° for one hour. The product, boiled with water to remove acid and unchanged naphthalene, may be freed from dinitronaphthalene, if present, by extraction with carbon disulphide (*cf.* Beilstein and Kuhlberg, Annalen, 1873, 169, 81).

On the large scale, finely powdered naphthalene (2·5 pts.) is added gradually through a sieve to a mixture of nitric acid of sp.gr 1·38 (2 pts), sulphuric acid (2 pts), and spent acid from a previous operation (6 pts); the temperature being maintained at 45°–50° throughout the operation, and the nitration completed in one day When cold, the spent acid is run off from the solid cake of nitronaphthalene, and the latter, after being washed with hot water, is either granulated by allowing it to flow in a thin stream into cold water (Witt, Chem Ind. 1887, 10, 216) or crystallised from solution in one-fourth its weight of solvent naphtha (Paul, Z. angew. Chem. 1897, 10, 146). The nitration can be effected by mixing naphthalene with powdered nitre, and stirring the mixture into sulphuric acid (Höchst, D. R.-P. 201623). To avoid the use of sulphuric acid, and yet admit of the employment of a weaker nitric acid (sp.gr. below 1·33) than will attack naphthalene in its absence, an electrolytic method has been proposed (Tryller, D. R -P. 100417).

Identification.—It crystallises in long, slender, lustrous needles, m.p. 61° (Aguiar, Ber. 1872, 5, 371), b.p. 304° (Koninck and Marquart, *ibid.* 12), sp.gr. 1·33, and is practically non-volatile with steam. It is readily soluble in benzene and its homologues, carbon disulphide, ether, or hot alcohol: in 87·5 p.c. alcohol, 1 pt. dissolves in 35·6 pts. at 15°. It is not an explosive; its vapour attacks the eyes and it is poisonous.

Reactions.—With chromic acid in acetic acid solution it is oxidised to 3-*nitrophthalic acid* (Beilstein and Kurbatow, Annalen, 1880, 202, 217); with 5 p.c. potassium permanganate to 3-*nitrophthalonic* and 3-*nitrophthalic acids* (Friedländer and Weisberg, Ber. 1895, 28, 1642); but with cupric or ferric oxide and caustic soda solution at 250° to a mixture of *phthalic* and *benzoic acids* (Bindsch., D. R.-P. 136410; 140999; Eng. P. 15527 of 1901).

When boiled with ammonium sulphite solution it is converted into a mixture of α-*naphthylamine-sulphamic* and 4-*sulphonic acids*, but with sodium bisulphite solution into α-*naphthylamine-2 : 4-disulphonic acid* mixed with a small amount of the 4-monosulphonic acid. Reduction in acid solution converts it into α-*naphthylamine*. With excess of hydrogen, in contact with finely divided copper at 330°–350°, it also gives α-*naphthylamine*, but with nickel at this temperature not only α-naphthylamine but tetrahydronaphthalene ammonia and naphthalene are produced (Sabatier and Senderens, Compt rend. 1902, 135, 226). In alcoholic solution with sodium amalgam, *azoxynaphthalene* is formed (Jaworsky, J pr. Chem. 1865, 94, 285).

By chlorination a mixture of 5- and 8-*chloro-α-nitronaphthalenes* is obtained. On sulphonation with anhydro-acid it yields a mixture of the α-*nitronaphthalene* 5-, 6-, and 7-*sulphonic acids*, the first named being the chief product.

(ii.) β-**Nitronaphthalene.** The isolation of β-nitronaphthalene from crude mononitronaphthalene has yet to be confirmed although its production in the nitration of naphthalene has long been thought probable from the fact that technical α-naphthylamine contains β-naphthylamine in small quantity (Reverdin and Noelting, Sur la constitution de la naphtaline et de ses dérivés, ed. 1888, 33; Erdmann, Annalen, 1893, 275, 217; Weiler-ter-Meer, D. R.-P. 205076; Eng. P. 16446 of 1907; *cf.* however, Witt, Chem. Ind. 1887, 10, 220; Cain, Intermed. Prod. for Dyes, 2nd ed. p. 185, footnote; Tetralin Co., D. R.-P. 332593).

In contrast with naphthalene, tetralin (tetra-hydronaphthalene) furnishes a mixture of α- and β-mononitrotetralin, and from the latter β-nitronaphthalene has been prepared (Tetralin Co., D. R.-P. 332593).

Preparation.—It can be obtained from 2-nitro-α-naphthylamine by the diazo-reaction (Lellmann and Remy, Ber. 1886, 19, 236; Lellmann, Ber. 1887, 20, 891); in 7 p.c. yield from β-diazonaphthalene nitrite by treatment with cuprous oxide (Sandmeyer, Ber. 1887, 20, 1496); and, in 25 p.c. yield, from diazotised β-naphthylamine sulphate by interaction with cuprocupric sulphite and potassium nitrite solution at the ordinary temperature (Hantzsch and Blagden, Ber. 1900, 33, 2554).

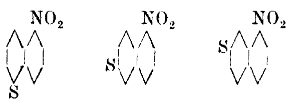
Identification.—It crystallises from dilute alcohol in small yellow needles, melts at 79°, has an odour of cinnamon, and volatilises only slowly with steam.

Reactions.—On sulphonation, it yields a mixture of β-*nitronaphthalene*-5- and 8-*sulphonic acids*. By reduction in acid solution it furnishes β-*naphthylamine*. When warmed with methyl alcoholic potash it gives 2-*nitroso-α-naphthol.*

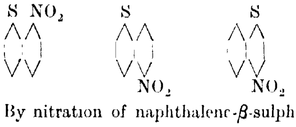
NITRONAPHTHALENEMONOSULPHONIC ACIDS.

Introductory.—The six nitronaphthalenemonosulphonic acids which are known with certainty are α-nitro-compounds, and are obtained either by the sulphonation of α-nitronaphthalene, or by the nitration of naphthalene-α- or β-monosulphonic acid. The products from each of these sources are :

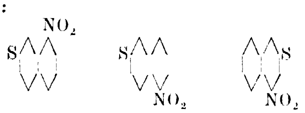
(a) By sulphonation of α-nitronaphthalene :



(b) By nitration of naphthalene-α-sulphonic acid [1]



(c) By nitration of naphthalene-β-sulphonic acid :



The separation of the isomeric acids obtained by these methods is not easy, and for technical purposes is not attempted, as the naphthylaminesulphonic acids, for the production of which they are made, can be isolated from the respective reduction products with much less difficulty.

On comparing these products of the nitration of naphthalenemonosulphonic acids with those of naphthalene-di- and tri-sulphonic acids (*v.* pp. 431, 432), it will be noticed that the former always, but the latter only rarely, furnish isomerides; also that the NO_2 group can assume the 1 : 4-(*para-*) or the 1 : 8-(*peri-*) but not the 1 : 2-(*ortho-*) position relatively to the SO_3H group.

(i.) α-**Nitronaphthalene-3-sulphonic acid** (Cleve's [γ-]*nitronaphthalenesulphonic acid*),[2] formed in small amount when sodium naphthalene-β-sulphonate is nitrated (*v.* the 6-sulphonic acid), is obtained from the sulphonyl chloride by boiling it with water (Cleve, Ber. 1886, 19, 2179; *cf* Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 239).

Identification.—The *lead* salt PbA_2+3H_2O, *barium* salt BaA_2+3H_2O, and *potassium* salt KA, crystallise in sparingly soluble needles. The *chloride* forms needles, m.p. 140°, convertible into 1 : 3-*dichloronaphthalene.* Reduction converts the acid into α *naphthylamine-3-sulphonic acid* (Cleve, *l c.*).

(ii.) α-**Nitronaphthalene-4-sulphonic acid**, formed in small quantity by the nitration of sodium naphthalene-α-sulphonate (*v.* the 8-sulphonic acid), is isolated from the product by means of its chloride (Cleve, Ber. 1890, 23, 959).[3]

Identification.—The *barium* salt, BaA_2+H_2O, forms needles soluble in 66 parts of cold and 33 parts of boiling water; the *calcium* salt, CaA_2+2H_2O, scales soluble in 37 parts of water at 17° and 16 parts at 100°; the *potassium* salt, KA, needles; and the *sodium* salt, $NaA+H_2O$, needles. The *chloride* forms prisms, m.p. 99°. Reduction converts the acid into α-*naphthylamine-4-sulphonic acid* (Cleve, *l.c.*).

(iii.) α-**Nitronaphthalene-5-sulphonic acid** (*Cleve's* [α-]*acid*) is obtained as chief product (about 80 p.c.) when α-nitronaphthalene is sulphonated with anhydro-acid; but as minor product (20–30 p.c.; *v.* the 8-sulphonic acid) when sodium naphthalene-α-sulphonate is nitrated. It is said to be the only product of the interaction of α-nitronaphthalene and chlorosulphonic acid (Armstrong and Williamson, Chem. Soc. Proc. 1886, 2, 233).

Preparation.—(1) Finely divided dry α-nitronaphthalene (20 pts.) is added to a mixture of sulphuric acid (35 pts.), and 24 p.c. anhydro-acid (25 pts.) at such a rate that the temperature does not rise above 90°, and the mixture maintained at this temperature during 8 hours or until sulphonation is complete. The product, poured on to an equal weight of ice, gives a crystalline separation of the pure 5-sulphonic acid (Witt, Chem. Ind. 1887, 10, 218). From the mother liquor, the isomeric 6- and 7-sulphonic acids can be isolated by conversion into and fractional crystallisation of the nitronaphthalenesulphonyl chlorides (Palmaer, Ber. 1888, 21, 3260).

(2) The formation of dark resinous substances, unavoidable when α-nitronaphthalene is sulphonated by anhydro-acid, does not occur if fused salt is added to the acid in quantity sufficient to convert the dissolved anhydride into chlorosulphonic acid. Following this modified process, α-nitronaphthalene (10 pts.) is added to the mixed sulphuric and chlorosulphonic acids obtained from 20 p.c. anhydro-acid (26 pts.), and the mixture heated on a water-bath until sulphonation is complete (Erdmann, Annalen, 1888, 247, 315).

Identification.—The *acid*, $HA+4H_2O$, crystallises in easily soluble pale yellow needles; the *lead* salt, PbA_2+3H_2O, in scales; and the *barium* salt, BaA_2+3H_2O, in sparingly soluble needles (Cleve, Bull. Soc. chim. 1875, [ii.] 24, 510). The *calcium* salt, CaA_2+2H_2O, forms sparingly soluble needles; the *potassium* salt, $KA+H_2O$, hexagonal tables soluble in 25 parts of water at 17° (Erdmann, Annalen, 1893, 275, 247); the *sodium* salt, $NaA+\frac{1}{2}H_2O$, very soluble tables (Cleve, *l.c.*). The *chloride* needles, m.p. 113°, is convertible into 1 : 5-*dichloronaphthalene* (Cleve, *l.c.*).

Reactions.—Reduction in acid solution converts it into *α-naphthylamine-5-sulphonic acid*; with sodium amalgam into *α-naphthylamine* (Claus, Ber. 1877, 10, 1303); and electrolytically into 1-*amino-4-naphthol-5-sulphonic acid*, doubtless by transformation of the hydroxylamine first formed (*cf.* Fierz and Weissenbach, Helv. Chim. Acta. 1920, 3, 305). Nitration furnishes 1 : 8-*dinitronaphthalene-5-sulphonic acid.*

(iv.) α-**Nitronaphthalene-6-sulphonic acid** (*Cleve's* [θ]*acid.* A mixture of this acid with about an equal quantity of the 7-sulphonic acid forms almost the entire product of the nitration of sodium naphthalene-β-sulphonate, the 3-sulphonic acid being present only in very small amount. A mixture of the 6- and 7-sulphonic acids constitutes the minor product of the sulphonation of α-nitronaphthalene (*v.* the 5-sulphonic acid).

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[1] According to Friedländer (Heumann, Anilinfarben, 1898, ii, 517), β-nitronaphthalene-4-sulphonic acid occurs in small quantity in the product from this source, but no description of the acid has been given.

[2] In every case where the constitution of an α-nitronaphthalenesulphonic acid is given, the nitro-group is supposed to be in the position '1.'

[3] Erdmann and Suvern did not succeed in finding this acid among the nitration products of naphthalene-α-sulphonyl chloride (Annalen, 1893, 275, 249).

Preparation.—(1) Sodium naphthalene-β-sulphonate (23 pts.) is stirred into sulphuric acid (115 pts.) at a temperature not exceeding 30°, the whole cooled to 0°, and a mixture of nitric acid (7 pts. HNO_3) and sulphuric acid then added at 0°–10°, the nitration being completed at this temperature. After removal of the excess of sulphuric acid by lime, the filtrate is used either for the isolation of the 6- and 7-sulphonic acids or for their reduction to the corresponding α-naphthylaminesulphonic acids (Cassella, D. R.-P. 67017; Eng. P. 6972 of 1891; *cf.* D. R.-P. 85058).

(2) Sodium naphthalene-β-sulphonate is stirred into cold nitric acid of sp.gr. 1·3, the mixture warmed to complete the nitration, and the product converted into barium salt. By extraction of this salt with boiling water, the greater part of the sparingly soluble 6-sulphonate remains undissolved. To separate the remainder the filtrate, which in addition contains the 7- and 3-isomerides, is evaporated to dryness, the residue converted into chloride, and this extracted by carbon disulphide, in which the 7-sulphonyl chloride is only sparingly soluble. The 6- and the 3-sulphonyl chlorides are then separated by fractional crystallisation from the solution (Cleve, Bull. Soc. chim. 1876, [ii.] 26, 444; 1878, [ii.] 29, 414; Ber. 1886, 19, 2179; *cf.* Erdmann and Suvern, Annalen, 1893, 275, 251).

Identification.—The *acid* crystallises in readily soluble brown needles; the *barium* salt BaA_2+H_2O in needles soluble in 782 parts of water at 22°; the *calcium* salt CaA_2+H_2O in scales; the *potassium* salt KA in tables soluble in 29 parts of water at 20°; the *sodium* salt $NaA+3H_2O$ in crusts consisting of scales. The *chloride* forms prisms, m.p. 125·5°, convertible into 1 : 6-*dichloronaphthalene* (Cleve, *l.c.*).

Reactions.—Reduction in acid solution converts it into *α-naphthylamine-6-sulphonic acid*, and electrolytically into 1-*amino-4-naphthol-6-sulphonic acid* (*cf.* Fierz and Weissenbach, *l.c.*). Nitration furnishes 1 : 8-*dinitronaphthalene-6-sulphonic acid.*

(v.) α-**Nitronaphthalene-7-sulphonic acid** (*Cleve's* [θ-] or [δ-]*nitronaphthalenesulphonic acid* [1]) constitutes about one-half of the product when either sodium naphthalene-β-sulphonate (*v.* the 6-sulphonic acid; *cf.* Cassella, D. R.-P. 85058), or naphthalene-β-sulphonyl chloride (Erdmann and Suvern, Annalen, 1893, 275, 238) is nitrated, but is formed only in small amount when α-nitronaphthalene is sulphonated (*v.* the 5-sulphonic acid).

Identification.—The *acid* forms brown needles, very soluble in water, but, unlike the 6-sulphonic acid, is almost insoluble in concentrated hydrochloric acid, and less soluble than it in 33 p.c. sulphuric acid. The *barium* salt $BaA_2+3\frac{1}{2}H_2O$ forms granular aggregates of needles, soluble, when anhydrous, in 377 parts of water at 17° but in 9·1 parts of boiling water; the *calcium* salt, very soluble needles; the *potassium* salt $KA+\frac{1}{2}H_2O$, needles readily soluble in water; the *sodium* salt, spherical aggregates of needles (Palmaer, Ber. 1888, 21, 3261). The *chloride* forms prisms, m.p. 169°, convertible into 1 : 7-*dichloronaphthalene* (Cleve, Bull. Soc. chim. 1878, [ii.] 29, 414; Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 19).

Reactions.—Reduction in acid solution converts it into *α-naphthylamine-7-sulphonic acid*, and electrolytically into 1-*amino-4-naphthol-7-sulphonic acid* (*cf.* Fierz and Weissenbach, *l.c.*). Nitration furnishes 1 : 5-*dinitronaphthalene-7-sulphonic acid.*

(vi.) α-**Nitronaphthalene-8-sulphonic acid** is obtained as chief product (60–70 p.c.; *v.* the 5-sulphonic acid) when sodium naphthalene-α-sulphonate is nitrated.

Preparation.—(1) Sodium naphthalene-α-sulphonate (4 pts.) is stirred into nitric acid of sp.gr. 1·45 (5 pts.), and the product converted into calcium salt. From the solution of the calcium salt, the greater part of the 5-sulphonate is separated by concentration, the more soluble 8-sulphonate being contained in the mother liquors (Cleve, Ber. 1890, 23, 958). For technical purposes the separation is unnecessary, as the corresponding naphthylaminesulphonic acids differ to a much greater degree in solubility, and are more easily isolated (*cf.* Schollkopf, D. R.-P. 40571; Eng. P. 15775 of 1885).

(2) The acid can be obtained by stirring naphthalene-α-sulphonyl chloride into 3 times its weight of nitric acid of sp.gr. 1·475 at −5°; extracting the α-nitronaphthalene-4- and 5-sulphonyl chlorides from the product by carbon disulphide, in which the 8-isomeride is almost insoluble, and hydrolysing the residue (Erdmann and Suvern, Annalen, 1893, 275, 237; *cf.* Reissert, Ber. 1922, 55, 862).

Identification.—The *acid* forms needles: the *barium* salt $BaA_2+2\frac{1}{2}H_2O$, crusts; the *calcium* salt $CaA_2+4\frac{1}{2}H_2O$, scales; the *potassium* salt $KA+H_2O$, needles, or $KA+2\frac{1}{2}H_2O$, scales, all easily soluble in water. The *chloride* forms prisms, m.p. 161° (Erdmann and Süvern, *l.c.*). Reduction converts the acid into *α-naphthylamine-8-sulphonic acid.*

(vii and viii.) β-**Nitronaphthalene-5-sulphonic acid**, mixed with the 8-**sulphonic acid**, is obtained by sulphonating β-nitronaphthalene with ice-cooled anhydro-acid, and separated from it by fractional crystallisation of the mixed chlorides from benzene. The 5-*sulphonyl chloride*, prisms, m.p. 127°, is more soluble in benzene than the 8-*sulphonyl chloride*, needles, m.p. 169°–170° (Kappeler, Ber. 1912, 45, 634).

NITRONAPHTHALENEDISULPHONIC ACIDS.

Introductory.—The nitronaphthalenedisulphonic acids are obtained for the most part from naphthalenedisulphonic acids by nitration. With two of these acids, *viz.* the naphthalene-1 : 5- and 1 : 6-disulphonic acids, both α- and β-nitro-derivatives are formed, the α-nitrodisulphonic acid being the chief product:—

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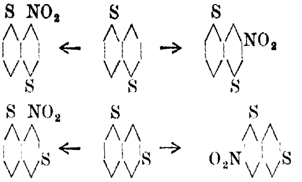
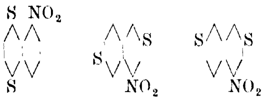
[1] This acid was originally termed [δ-] by Cleve, and is so described in his communication to the Paris Chemical Society (Bull. Soc. chim. 1878, [ii.] 29, 414). In the Swedish paper (Forhandl. 1878, 2, 32), which is practically identical with the French, the term [θ-] is employed, since 'the acid yields a new dichloronaphthalene which being the eighth known is distinguished as θ.'



but with each of the 1 : 4-, 2 : 6-, and 2 : 7-disulphonic acids only one, and that the α-nitro acid, has been isolated :—



(i.) α-**Nitronaphthalene**-3 : 6-**disulphonic acid** (*Alén's* [α-]*acid* ; *Freund's acid* [1]) is obtained by nitrating sodium naphthalene-2 : 7-disulphonate (33 pts.), dissolved in sulphuric acid (50 pts.), with 50 p.c. nitric acid (25 pts.) in the cold. Or, if the product is to be used for reduction—as the presence of α nitronaphthalene-3 · 7-disulphonic acid is then of no consequence—the melt, which also contains naphthalene-2 : 6-disulphonic acid, obtained by sulphonating naphthalene (1 pt.) with sulphuric acid (5 pts.) at 160° for 8 hours, is nitrated with 50 p.c. nitric acid (2 pts) in the cold (Freund, D. R.-P. 27346 ; Eng. P. 1069 of 1883 ; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 82). Its chloride is formed, together with the 1 : 8-dinitronaphthalene-3 : 6-disulphonyl chloride by nitrating naphthalene-2 : 7-disulphonyl chloride with nitrosulphuric acid at the ordinary temperature (Alén, Bull. Soc. chim. 1883, [ii.] 39, 63).

Identification.—The *acid* and salts crystallise in small needles ; the *barium* salt $BaA+5H_2O$, is sparingly ; the *potassium* salt K_2A+3H_2O and *sodium* salt Na_2A+6H_2O are readily soluble in water. The *chloride* forms needles, m.p. 140°–141°, convertible into 1 · 3 : 6 *trichloronaphthalene* (Alén, Förhandl. 1884, 2, 95 ; Cleve, Ber. 1892, 25, 2487 ; Armstrong and Wynne, *l.c.*).

Reactions.—Reduction in acid solution converts it into *α-naphthylamine*-3 : 6-*disulphonic acid*, and electrolytically into 1-*amino*-4-*naphthol*-3 : 6-*disulphonic acid.* With sodium amalgam it gives *α-naphthylamine* (Alén, Forhandl. 1883, 8, 3).

(ii.) α-**Nitronaphthalene**-3 : 7-**disulphonic acid** (*Alén's* [β-]*acid*) is obtained by nitration of naphthalene-2 · 6-disulphonic acid, as described for the 3 : 6-disulphonic acid (Freund, *l.c.*). Its chloride is formed, as sole product, when naphthalene-2 : 6-disulphonyl chloride is nitrated with nitrosulphuric acid (Alén, Bull. Soc. chim. 1883, [ii.] 39, 64).

Identification—The *barium* salt $BaA+2H_2O$, tablets ; *calcium* salt $CaA+2H_2O$, needles ; *potassium* salt K_2A, needles ; and *sodium* salt Na_2A+2H_2O, needles, are less soluble than the salts of the 3 : 6-acid. The *chloride* (with 1 mol. C_6H_6 from benzene), forms prisms, m.p. 190°–192°, convertible into 1 : 3 : 7-*trichloronaphthalene* (Alén, Förhandl. 1884, 2, 95 ; Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 13).

Reactions.—Reduction in acid solution converts it into *α-naphthylamine*-3 : 7-*disulphonic acid*, and electrolytically into 1-*amino*-4-*naphthol*-3 : 7-*disulphonic acid.* With sodium amalgam it gives *α-naphthylamine* (Alén, Forhandl. 1883, 8, 21).

(iii.) α-**Nitronaphthalene**-3 : 8-**disulphonic acid** is formed as chief product, together with some β-nitronaphthalene-4 : 7-disulphonic acid by nitrating naphthalene-1 : 6-disulphonic acid or its salts (Schultz, Ber. 1890, 23, 77 ; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27).

Preparation.—Sodium naphthalene-β-sulphonate (50 pts.), sulphonated with 2½–3 times its weight of 20 p.c. anhydro-acid at 100°, is cooled to 10°–15°, and nitrated below 25° with nitric acid of sp.gr. 1·4 (22·5 pts.) during about 2 hours (Ewer and Pick, D. R.-P. 52724). Or, the product obtained by sulphonating either naphthalene (10 pts.) with monohydrate (40 pts.), first at 80°–95° and then for 10 hours at 110°, or naphthalene-β-sulphonic acid melt (20 pts.) with monohydrate (20 pts) at 110°, is nitrated below 25°–30° with 8·4 pts. of nitric acid of sp.gr. 1·38 (Badische, D. P. Anm. B. 9514 ; Bernthsen, Ber. 1889, 22, 3328).[2] Owing to their sparing solubility in alkalis or brine, the alkali salts of the nitro-acid are easily separated from the nitration product after dilution with water, but the separation is unnecessary if the nitro-acid is to be used for reduction to α-naphthylamine-3 · 8-disulphonic acid.

It is also obtained, together with α-nitronaphthalene-4 : 8-disulphonic acid and small quantities of the corresponding β-nitrodisulphonic acids, when the product formed by sulphonating naphthalene (10 pts.) with 23 p.c. anhydro-acid (50 pts) in the cold is cooled with ice and nitrated with nitric acid of sp.gr. 1·45 (7 pts.). This product is useful only for reduction to the amino-acids from which α-naphthylamine-3 : 8-disulphonic acid can easily be separated (Aktienges., D. R.-P. 45776 ; Eng. P. 4625 of 1888).

Salts.—The salts crystallise in easily soluble needles ; the *potassium* salt K_2A is almost insoluble in dilute caustic potash solution (Friedlander, Ber. 1895, 28, 1535).

Reactions.—Reduction in acid solution converts it into *α-naphthylamine*-3 : 8-*disulphonic acid*, but in neutral solution with sodium bisulphite it yields *α-naphthylamine*-3 : 6 : 8-*trisulphonic acid.* Digestion with concentrated caustic soda solution furnishes the basic sodium salt of 4-*nitroso α-naphthol*-2 : 5-*disulphonic acid.*

(iv.) α-**Nitronaphthalene**-4 : 8-**disulphonic acid** is obtained, together with the 3 : 8-disulphonic acid, when as already described a melt containing the naphthalene-1 : 5- and 1 : 6-disulphonic acids is nitrated (Aktienges., *l.c.*). It is also formed by nitrating naphthalene-1 : 5-disulphonic acid, and separated from the accompanying β-nitronaphthalene-4 : 8-disulphonic acid (*q.v.*) by means of brine, in which the sodium salt of the latter is the less soluble (Cassella, D. R.-P. 65997). Reduction converts it into *α-naphthylamine*-4 : 8-*disulphonic acid.*

(v.) α-**Nitronaphthalene**-5 : 8-**disulphonic acid** is formed when barium naphthalene-1 : 4-disulphonate (5 pts.), mixed with sulphuric acid (30 pts.), is nitrated at 10°–15° with 25 p.c. nitric acid (3 pts.). The product is free from isomerides (Bayer, D. R.-P. 70857; Gattermann, Ber. 1899, 32, 1156). Reduction in acid solution converts it into *a-naphthylamine-5 : 8-disulphonic acid.*

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[1] This acid, like the 3 : 7-disulphonic acid, was regarded by Freund as a β-nitronaphthalene derivative.

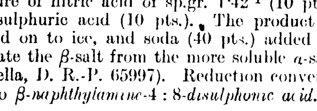
[2] According to Friedländer, the product obtained by any of these methods contains at least four nitro-acids, of which the α-nitronaphthalene-3 : 8-disulphonic acid constitutes only about 40 p.c. (Heumann, Anilinfarben, 1898, ii, 518).

(vi.) *β*-**Nitronaphthalene-4 : 7-disulphonic acid** is formed, together with *a* nitronaphthalene-3 : 8-disulphonic acid, by nitration of naphthalene-1 : 6-disulphonic acid (Schultz, Ber. 1890, 23, 77; Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27). Reduction converts it into *β-naphthylamine-4 : 7-disulphonic acid.*

(vii.) *β*-**Nitronaphthalene-4 : 8-disulphonic acid** is obtained when naphthalene-1 : 5-disulphonic acid (28 pts.), suspended in well-cooled sulphuric acid (90 pts.), is nitrated with a mixture of nitric acid of sp.gr. 1·42[1] (10 pts.) and sulphuric acid (10 pts.). The product is poured on to ice, and soda (40 pts.) added to separate the *β*-salt from the more soluble *a*-salt (Cassella, D. R.-P. 65997). Reduction converts it into *β-naphthylamine-4 : 8-disulphonic acid.*

Nitronaphthalenetrisulphonic Acids.

Three nitronaphthalenetrisulphonic acids are obtained from the corresponding naphthalenetrisulphonic acids by nitration



and two of them, the 3 : 6 : 8- and the 4 : 6 : 8-isomerides, are important in connexion with the manufacture of the H- and K- (aminonaphtholdisulphonic) acids.

(i.) *a*-**Nitronaphthalene-3 : 5 : 7-trisulphonic acid,** formed when sodium naphthalene-1 : 3 : 7-trisulphonate, dissolved in sulphuric acid, is nitrated at 15°–20°, can be separated by the addition of salt to the product after dilution with water (Cassella, D. R.-P. 75432) Reduction converts it into *a-naphthylamine-3 : 5 : 7-trisulphonic acid.*

(ii.) *a*-**Nitronaphthalene-3 : 6 : 8-trisulphonic acid** is obtained by the nitration of naphthalene-1 : 3 : 6-trisulphonic acid. For technical purposes, the melt obtained by sulphonating naphthalene-1 : 6- or 2 : 7-disulphonic acid is cooled to 25°–30°, and nitrated at this temperature with the calculated quantity of nitric acid (Koch, D. R.-P. 56058; Eng P. 9258 of 1890).

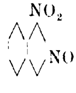
Salts.—The *lead* $Pb_3A_2+8H_2O$; *barium* $Ba_3A_2+8H_2O$; *sodium* Na_3A+6H_2O; and *aniline* $B_3A+2\frac{1}{2}H_2O$ salts crystallise in needles (Fierz and Schmid, Helv. Chim. Acta, 1921, 4, 381).

Reactions.—Reduction in acid solution converts it into *a-naphthylamine-3 : 6 : 8-trisulphonic acid.* Digestion with ammonia at 150°–170° furnishes *β-naphthylamine-3 : 6 : 8-trisulphonic acid,* nitrogen being eliminated

(iii.) *a*-**Nitronaphthalene-4 : 6 : 8-trisulphonic acid** is produced by the nitration of sodium naphthalene-1 : 3 : 5-trisulphonate, the trisulphonic acid melt formed by sulphonating naphthalene-1 : 5-disulphonic acid (1 mol.) with anhydro-acid being diluted to a density of 66°Bé. at 15°, cooled to 5°, and the calculated quantity of nitric acid (1 mol.) mixed with sulphuric acid added at this temperature (Bayer, D. P. Anm. F. 7004; Eng. P. 17141 c of 1893; *cf.* Kalle, D. P. Anm. K. 11104; D. R.-P. 82563; Eng. P. 1641 of 1894). Reduction converts it into *a-naphthylamine-4 : 6 : 8-trisulphonic acid.*

Dinitronaphthalenes

Introductory.—Two dinitronaphthalenes, the 1 : 5- and 1 : 8-compounds, are obtained when naphthalene or *a*-nitronaphthalene is nitrated with strong nitric acid or with a mixture of nitric and sulphuric acids. The proportion in which they are formed varies to some extent, but may be taken as 1 to 2 (Friedlander and Scherzer, Chem. Zentr. 1900, i., 410), although according to Gassmann, who used more concentrated acid mixtures, the best yield of 1 : 8-dinitronaphthalene (about 70 p.c.) is obtained only when the temperature beyond the stage of mononitration is the lowest possible (Ber. 1896, 29, 1241, 1521).



(i.) 1 : 3 - **Dinitronaphthalene** ([*γ*-]*dinitronaphthalene*) is prepared by boiling diazotised 2 : 4-dinitro-*a*-naphthylamine with alcohol. The statement that it is a product of the nitration of naphthalene (Hochst, D.R.-P. 96227; *cf.* Pictet, Compt Rend. 1893, 116, 815) was not confirmed by Friedlander (Ber. 1899, 32, 3531). It crystallises from dilute alcohol in bright yellow needles, m.p. 144° (Liebermann and Hammerschlag, Annalen, 1876, 183, 274; *cf.* Friedlander, Ber 1895, 28, 1951).

(ii.) 1 : 5 - **Dinitronaphthalene** ([*a*-]*dinitronaphthalene*) is obtained as minor product, together with the 1 : 8-compound, when *a*-nitronaphthalene (10 pts.) dissolved in sulphuric acid (60 pts.) is nitrated at 0° by a mixture of nitric acid of sp.gr. 1·4 (5·2 pts.) with sulphuric acid (26 pts.). The solution, at first red, becomes white owing to the separation of the mixed dinitronaphthalenes as a thick magma, which when dry melts at about 140°. To isolate its constituents, this solid product is not removed from the spent acid, but at the close of the nitration is heated with it at 80°–90° until completely dissolved and the solution then cooled to 20°, whereby an almost complete separation of the 1 : 5-isomeride is achieved. From the filtrate, the remainder of the nitration product is precipitated by the addition of water, and the 1 : 8-derivative extracted from the dried precipitate by pyridine in which 1 : 5-dinitronaphthalene is only sparingly soluble (Friedländer, Ber. 1899, 32, 3531; Kalle, D. R.-P. 117368). The removal of the 1 : 8-derivative can also be effected by extraction of the dry nitration product with acetone (Beilstein and Kurbatow, Annalen, 1880, 202, 219), chloroform (Darmstädter and Wichelhaus, Annalen, 1869, 152, 301), benzene (Aguiar, Ber. 1870, 3, 29; Beilstein and Kuhlberg, Annalen, 1873, 169, 85), or acetic acid (Aguiar, Ber. 1872, 5, 372).

Alternatively, the mixture of dinitronaphthalenes (200 pts.), obtained technically in the form of a 60 p.c. paste, is heated at 80°–90° during 5–6 hours with 40 p.c. sodium bisulphite solution (740 pts.) and 25 p.c. ammonia (140 pts.), and the insoluble 1 : 5-dinitronaphthalene then removed by filtration. In this case the filtrate contains not 1 : 8-dinitronaphthalene, but α-naphthylsulphamino-4 : 7-di- and 2 : 4 : 7-trisulphonic acids arising from the interaction of this dinitro- compound with the bisulphite (Höchst, D. R.-P. 221383).

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[1] In Cassella's patent, 90°Bé. is given, presumably a misprint for 40°Bé.

Properties.—1 : 5 - Dinitronaphthalene crystallises from acetic acid in six-sided yellow needles, m.p. 216° (Aguiar, Ber. 1872, 5, 372). It is only sparingly soluble in the ordinary solvents, and practically insoluble in carbon disulphide or cold nitric acid. With phosphorus pentachloride it yields 1 : 5-*dichloronaphthalene* (Atterberg, Ber. 1876, 9, 1188, 1730).

Reactions.—Reduction with alcoholic ammonium sulphide converts it into 5-*nitro-α-naphthylamine* and 1 : 5-*diaminonaphthalene*, but in acid solution only the latter is obtained. Digestion with ammonium sulphite or sodium bisulphite solution furnishes 1 : 5-*diaminonaphthalenedisulphonic acid.*

When heated with 12–23 p.c. anhydro-acid at 40°–50° it yields 8-*nitro-1-nitroso-α-naphthol*, but if a reducing agent, such as sulphur or zinc be present, a *naphthazarin intermediate product* is formed from which naphthazarin (5 : 6-dihydroxy-[α-]naphthaquinone) can be isolated.

(iii.) 1 : 6 - **Dinitronaphthalene** ([δ-]*dinitronaphthalene*) is obtained by boiling diazotised 1 : 6-dinitro-β-naphthylamine with alcohol. It crystallises from alcohol in bright yellow needles, m.p. 161·5° (Graebe and Drews, Ber. 1884, 17, 1170; *cf.* Kehrmann and Matis, Ber. 1898, 31, 2419).

(iv.) 1 : 8 - **Dinitronaphthalene** ([β-]*dinitronaphthalene*) is the major product of the dinitration of naphthalene. For its purification, *v.* 1 : 5-dinitronaphthalene.

Properties. — 1 : 8 - Dinitronaphthalene crystallises in large, yellow rhombic plates, m.p. 170° (Aguiar, Ber. 1872, 5, 372). In ordinary solvents, and in concentrated sulphuric acid, it is more soluble than the 1 : 5-compound. According to Beilstein and Kuhlberg (Annalen, 1873, 169, 86), one part dissolves in 91·4 parts of chloroform, in 530 parts of 88 p.c. alcohol, or in 139 parts of benzene at 19° : and according to Friedländer (Ber. 1899, 32, 3531), 1 part dissolves in 10 parts of cold or in 1·5 parts of hot pyridine. With phosphorus pentachloride it yields 1 : 8-*dichloronaphthalene* in small quantity, the chief product being 1 : 4 : 8-*trichloronaphthalene* (Atterberg, Ber. 1876, 9, 1188, 1732).

Reactions.—Reduction in acid solution converts it into 1 : 8-*diaminonaphthalene*. Digestion with sodium [1] or ammonium sulphite solution at 70°–90°, the alkali set free being removed as formed, yields *α-naphthylsulphamino*-4 : 7-*di-* and 2 : 4 : 7-*trisulphonic acids* (whence by hydrolysis the corresponding α-naphthylaminesulphonic acids are obtained), but boiling with sodium bisulphite solution furnishes 1 : 8-*diaminonaphthalenetrisulphonic acid.*

When heated with 12–23 p.c. anhydro-acid at 40°–50°, it yields 5-*nitro-4-nitroso-α-naphthol*, but if it be heated with sulphuric [2] acid and reducing agents, such as aniline or tin or iron, or its solution in sulphuric acid be electrolysed, a *naphthazarin intermediate product* is formed isomeric with that obtained from 1 : 5-dinitronaphthalene.

DINITRONAPHTHALENEMONOSULPHONIC ACIDS.

(i.) 1 : 5-**Dinitronaphthalene**-3- (or 7-) **sulphonic acid** is obtained when α-nitronaphthalene-7-sulphonic acid, dissolved in sulphuric acid, is nitrated at 0°–15°, and common salt added to the product after dilution with water (Cassella, D. R.-P. 85058). It is also stated to be formed when 1 : 5-dinitronaphthalene, dissolved in 6 times its weight of monohydrate, is heated at 100°–110° with rather more than twice its weight of 20 p.c. anhydro-acid (Höchst, D. R.-P. 117268), but according to Eckstein this dinitronaphthalene is not sulphonated by 15–25 p.c. anhydro-acid at 140°, and at higher temperatures or with stronger acid is destroyed (Ber. 1902, 35, 3403).

Identification.—The *sodium* salt forms needles, soluble in 12 parts of boiling water; the *chloride* prisms, m.p. 118° (Höchst, *l.c.*).

Reactions.—Reduction converts it into 1 : 5-*diaminonaphthalene-3-sulphonic acid*, but digestion with sodium sulphite or bisulphite solution gives a *nitro-α-naphthylaminesulphonic acid*. With anhydro-acid in presence of a reducing agent, a soluble blue 'intermediate product' is obtained which yields a *naphthazarinsulphonic acid* when boiled with water.

(ii.) 1 : 8-**Dinitronaphthalene**-3- (or 6-) **sulphonic acid** is formed, together with the 1 : 5-dinitro-acid, when sodium naphthalene-β-sulphonate, dissolved in sulphuric acid, is dinitrated below 10°, and is precipitated by stirring the product into twice its volume of brine, the 1 : 5-isomeride remaining in solution (Cassella, D. R.-P. 67017; Eng. P. 6972 of 1891; D. R.-P. 85058). It is also produced when 1 : 8-dinitronaphthalene, dissolved in monohydrate, is sulphonated at 100°–110° with twice its weight of 20 p.c. anhydro-acid (Höchst, D. R.-P. 117268; Eckstein, Ber. 1902, 35, 3403).

Identification.—The *barium* salt BaA_2+5H_2O soluble in 8·5 parts of boiling or 20 parts of cold water (Eckstein, *l.c.*); the *calcium* salt CaA_2+2H_2O; the *potassium* salt and the *sodium* salt $NaA+H_2O$, soluble in 6·5 parts of boiling water, crystallise in needles. The *chloride* forms monoclinic prisms, m.p. 143°–144° (Höchst, *l.c.*; *cf.* Hellstrom, Forhandl. 1888, 10, 613).

(iii.) 1 : 8-**Dinitronaphthalene**-4- (or 5-) **sulphonic acid** is formed when the monosulphonation product of α-nitronaphthalene, consisting chiefly of the 5-sulphonic acid, is nitrated at

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[1] Blue, violet, or black dyestuffs are obtained when 1 : 8-dinitronaphthalene is heated with alkali, sodium bisulphite solution, and reducing agents, such as glucose (Badische, D. R.-P. 79208; Eng. P. 10996 of 1893; D. R.-P. 88236; Eng. P. 7766 of 1896), milk sugar, sodium stannite, or sodium sulphide (Badische, D. R.-P. 92471; Eng. P. 20250 of 1896); or, omitting alkali, with sodium sulphide (Badische, D. R.-P. 84989; Eng. P. 10996 of 1893; D. R.-P. 88847; Eng. P. 22603 of 1894), or sodium disulphide (Höchst, D. R.-P. 117188, 117189).

[2] If sulphuretted hydrogen or antimony sulphide be used with the sulphuric acid, black dyestuffs are formed, which by interaction with sodium thiosulphate give violet shades (Badische, D. R.-P. 114264; Eng. P. 890 of 1900; D. R.-P. 147945; Eng. P. 1864 of 1903).

15°–20°, and the 1 : 8-dinitro-acid separated by stirring the mixture into brine (Cassella, D. R.-P. 70019; Eng. P. 4613 of 1893).

(iv.) 2 : 4 - **Dinitronaphthalene** - 8 - **sulphonic acid** is obtained when naphthasultam or 2 : 4-dinitronaphthasultam is heated with fuming nitric acid (Dannerth, J. Amer. Chem. Soc. 1907, 29, 1327).

DINITRONAPHTHALENEDISULPHONIC ACIDS.

(i.) 1 : 5-**Dinitronaphthalene**-3 . 7-**disulphonic acid** is obtained when sodium naphthalene-2 : 6-disulphonate (or α-nitronaphthalene-3 : 7-disulphonate), dissolved in sulphuric acid, is dinitrated (or nitrated) at 20°–30°, and the product salted out (Cassella, D. R.-P. 61174; Eng. P. 15346 of 1890; *cf.* Oehler, D. P. Anm. O. 1430; Bayer, D. R.-P. 126198).

Reactions.—Reduction in acid solution converts it into 1 : 5-*diaminonaphthalene*-3 : 7-*disulphonic acid.* When dissolved in monohydrate and heated at 50° with a solution of sulphur in 20 p.c anhydro-acid, it gives a blue mordant dye of the naphthazarin 'intermediate product' type (Bayer, *l.c.*).

(ii.) 1 : 6-**Dinitronaphthalene**-3 : 8-**disulphonic acid,** obtained by nitration of α-nitronaphthalene-3 : 8-disulphonic acid or of naphthalene-1 : 6-disulphonic acid has not been characterised. Reduction in acid solution converts it into 1 : 6-*diaminonaphthalene*-3 : 8-*disulphonic acid* (Friedländer and Kielbasinski, Ber. 1896, 29, 1982).

(iii.) 1 : 6 - **Dinitronaphthalene** - 4 : 8 - **disulphonic acid** is obtained when sodium naphthalene-1 : 5-disulphonate (or its mononitration product), dissolved in monohydrate, is dinitrated (or nitrated) below 30°. The product is free from isomerides (Kalle, D. R.-P. 72665), and on reduction in acid solution yields 1 : 6-*diaminonaphthalene*-4 : 8-*disulphonic acid* (Friedlander and Kielbasinski, *l.c.*).

(iv.) 1 : 8-**Dinitronaphthalene**-3 : 6-**disulphonic acid** is obtained free from isomerides when sodium naphthalene-2 : 7-disulphonate, dissolved in sulphuric acid, is dinitrated at 20°–30° (Cassella, D. R.-P. 67062; Eng. P. 1742 of 1891; Bayer, D. R.-P. 69190; Eng. P. 11522 of 1892). Its chloride is formed, together with the mononitro-derivative, by nitrating naphthalene-2 : 7-disulphonyl chloride (Alén, Förhandl. 1883, 8, 13).

Identification.—The *barium* salt $BaA+5H_2O$ prisms, and the *potassium* salt needles, K_2A from hot, or K_2A+4H_2O from cold solution, are easily soluble. The *chloride* has m.p. 219°; with 1 mol. C_6H_6 it forms needles (Alén, *l.c.*).

Reactions.—Reduction in acid solution converts it into 1 : 8-*diaminonaphthalene*-3 : 6-*disulphonic acid,* but digestion with sodium sulphite or bisulphite solution gives 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid.* With dilute caustic soda solution in the cold, it forms *sodium* 5-*nitro*-4-*nitroso*-α-*naphthol*-2 : 7-*disulphonate,* but 4 : 5-*dinitrosodihydroxynaphthalene*-2 : 7-*disulphonate* if the solution be concentrated.

TRINITRONAPHTHALENES.

Three trinitronaphthalenes, the 1 : 2 : 5-, 1 : 3 : 5-, and 1 : 4 : 5-derivatives, are obtained by the nitration of 1 : 5-dinitronaphthalene, and a fourth, the 1 : 3 : 8-derivative, by the nitration of 1 : 8-dinitronaphthalene. The constitution of these compounds has been determined by oxidation to the respective nitrophthalic acids.

Melting-point curves of the various binary and ternary mixtures of α-nitronaphthalene, 1 : 5- and 1 : 8-dinitronaphthalenes, and 1 : 2 : 5-, 1 : 3 : 5-, 1 : 3 : 8-, and 1 : 4 : 5-trinitronaphthalenes have been determined by Pascal and the results applied to the analysis of the products of the nitration of naphthalene (Bull. Soc. chim. 1920, [iv.] 27, 388).

(i.) 1 : 2 : 5 - or [δ-]**Trinitronaphthalene** (Will, Ber. 1895, 28, 377) crystallises from alcohol in needles, m.p. 112°–113°.

(ii.) 1 : 3 : 5 - or [α-]**Trinitronaphthalene** (Aguiar, Ber. 1872, 5, 373, 897) crystallises from alcohol in scales, m.p. 122°.

(iii.) 1 : 4 : 5 - or [γ-]**Trinitronaphthalene** (Beilstein and Kuhlberg, Annalen, 1873, 169, 97; *cf.* Will. *l.c.*) crystallises from chloroform in bright yellow scales, m.p. 154° (Aguiar, *l c.* 903)

(iv.) 1 : 3 : 8 - or [β-]**Trinitronaphthalene** (Beilstein and Kuhlberg, *l c.*; Friedländer, Ber. 1899, 32, 3531). From the mixed dinitronaphthalenes obtained by the nitration of α-nitronaphthalene (10 pts.), the greater part of the 1 : 5-derivative can be separated by Kalle's method as already described (*v.* 1 : 5-dinitronaphthalene). The mother liquor contains mainly the 1 : 8-derivative, and, by the addition of a mixture of nitric acid of sp.gr. 1·4 (3·3 pts.) with sulphuric acid (10 pts.) gives a crystalline separation of 1 : 3 : 8-trinitronaphthalene in needles, m.p. 218° (Kalle, D. R.-P. 117638). It dissolves in cold sodium bisulphite solution without undergoing change, but is converted into *nitroaminonaphtholsulphonic acids* when the solution is warmed (Friedlander and Scherzer, Chem. Zentr. 1900, i., 410).

TETRANITRONAPHTHALENES.

Five tetranitronaphthalenes have been described, three being obtained from 1 : 5- and two from 1 : 8-dinitronaphthalene:

(i.) [α-]**Tetranitronaphthalene,** which melts at 259° (Beilstein and Kuhlberg, Annalen, 1873, 169, 99; Aguiar, Ber. 1872, 5, 374);

(ii.) 1 : 2 : 5 : 8- or [δ-]**Tetranitronaphthalene,** which decomposes at about 300° without fusion (Will, Ber. 1895, 28, 369); and

(iii.) 1 : 3 : 5 : 8- or [γ-]**Tetranitronaphthalene,** which melts at 194°–195° (Will, *l.c.*).

(iv.) 1 : 2 : 6 : 8-**Tetranitronaphthalene,** which does not melt below 300° (Dhar, Chem. Soc. Trans. 1920, 117, 1004); and

(v.) 1 : 3 : 6 : 8- or [β-]**Tetranitronaphthalene,** which melts at 203° (Aguiar, *l.c.*; Will, *l.c.*).

CHLORONITRONAPHTHALENES.

Introductory.—By nitration α-chloronaphthalene yields seven nitro-derivatives. Of these three are mononitro-α-chloronaphthalenes, containing the nitro-group respectively in the α-positions 4, 5 and 8; two are dinitro-α-chloronaphthalenes with the nitro-groups respectively in the α-positions 4 : 5 and 4 : 8; and two are trinitro-α-chloronaphthalenes with the nitro-groups respectively in the positions 2 : 4 : 5 and 2 : 4 : 8. As in the case of 4- or *p*-nitrochlorobenzene, those chloronitronaphthalenes which contain NO_2 in the 4- or *para*-position relatively to Cl exchange the Cl for the NH_2 or OH radicle by interaction with ammonia or caustic alkali respectively.

By chlorination, mononitronaphthalene-α-sulphonic acids furnish chloronitronaphthalenes, Cl replacing the SO_3H group (Friedlander, Karamessinis and Schenk, Ber. 1922, 55, 45).

(i.) **4-Chloro-α-nitronaphthalene**, formed from 4-nitro-α-naphthylamine by the Sandmeyer reaction (Franzen and Helwert, Ber. 1920, 53, 320) is obtained as chief product, mixed with some of the 5-chloro- and a small quantity of the 8-chloro-α-nitronaphthalene, when α-chloronaphthalene is nitrated with nitric acid of sp.gr. 1·4 in the cold (Atterberg, Ber. 1876, 9, 927; Griesheim, D. R.-P. 120585). It crystallises in yellow needles, m.p. 85°.

Reactions.—Digestion with 8 p.c. alcoholic ammonia at 170° converts it into *4-nitro-α-naphthylamine*, and with solutions of alkali hydroxides, carbonates or acetates at 150° into *4-nitro-α-naphthol.*

(ii.) **8-Chloro-α-nitronaphthalene** is obtained as chief product, mixed with 5-chloro-α-nitronaphthalene (m.p. 111°) when α-nitronaphthalene is chlorinated at 40°–60° in the presence of ferric chloride, and separates as a crystalline magma from the product (Aktienges., D. R.-P. 99758; Ullmann and Consonno, Ber. 1902, 35, 2808). It forms needles, m.p. 94°.

Reaction.—When heated with sulphuric acid at 80°, it is converted into *8-chloro-α-nitronaphthalene-5-sulphonic acid*, whereas 5-chloro-α-nitronaphthalene does not undergo sulphonation under these conditions (Aktienges., D. R.-P. 103980).

(iii.) 5 : 8-**Dichloro-α-nitronaphthalene** has also been prepared by chlorinating α-nitronaphthalene in the presence of a carrier. It melts at 94° and on reduction gives 5 : *8-dichloro-α-naphthylamine* (Bayer, D. R.-P. 293318).

(iv.) **4-Chloro-1 : 3-dinitronaphthalene** is the product obtained when 2 : 4-dinitro-α-naphthol is heated with toluene-*p*-sulphonyl chloride in dimethylaniline at 80°. It forms iridescent yellow scales, m.p. 143°, and with aniline gives 2 : *4-dinitro-α-naphthylphenylamine* (Ullmann and Bruck, Ber. 1908, 41, 3932; D. R.-P. 199318).

(v.) **Dichloro-1 : 5-dinitronaphthalene**, also **chloro-** and **dichloro-1 . 8-dinitronaphthalene**, have been prepared by chlorinating the respective dinitronaphthalenes in a fused state in the presence of ferric chloride (Pollak, D. R.-P. 134306).

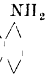
(vi.) **4-Chloro 1 : 3 · 8-trinitronaphthalene** is obtained, mixed with the 1 : 3 : 5- derivative, when α-chloronaphthalene is nitrated with nitric acid of sp.gr. 1·52, and separates from the product in hexagonal prisms, m.p. 143°–144°. The more soluble 1 : 3 : 5- compound, m.p. 118°–126°, has not been obtained pure. Both yield the corresponding *trinitro-α-naphthols* when heated with dilute caustic alkali solution (Kindl, Chem. Soc. Trans. 1913, 103, 1911).

IV. AMINO- DERIVATIVES.

Introductory.—The circumstance that nitration in the naphthalene series leads almost exclusively to the production of α- nitro- derivatives but sulphonation readily to the formation of β-sulphonic acids explains why methods for the preparation of α-naphthylamine and its sulphonic acids differ so completely from those employed in the case of β-compounds. α-Naphthylamine is obtained by the reduction of α-nitronaphthalene and several of the α-naphthylaminesulphonic acids are formed from α-nitronaphthalenesulphonic acids in the same way. But in the β- series, only two β-nitronaphthalenesulphonic acids are obtained by nitration—*viz.* the β-nitronaphthalene-4 : 7- and 4 : 8-disulphonic acids—and then only in relatively small amount, and it is to β-naphthol, itself produced from naphthalene-β-sulphonic acid, that β-naphthylamine and its derivatives owe their origin. β-Naphthol, when heated with ammonia under pressure with or without the use of dehydrating agents, but much more easily and in greater yield by digestion with ammonium bisulphite solution and ammonia at 100°–150°, is converted into β-naphthylamine, and by the use of similar methods β-naphtholsulphonic acids with certain exceptions, furnish the corresponding β-naphthylaminesulphonic acids.

The two naphthylamines and certain of their sulphonic acids are of much technical importance, being largely used as first, middle, or end components of azo- dyes: moreover, the sulphonic acids are also used in the manufacture of naphtholsulphonic acids, aminonaphtholsulphonic acids, or dihydroxynaphthalenesulphonic acids, which find extensive employment in the production of azo- dyes. The differences in the mode of coupling with diazotised bases in the two series has already been discussed (*v.* p. 417).

AMINONAPHTHALENES.



(i.) α-**Naphthylamine** (*1-aminonaphthalene; naphthalidam, naphthalidine*) is formed by the reduction of α-nitronaphthalene with alcoholic ammonium sulphide (Zinin, J. pr. Chem. 1842, 27, 141; *cf.* Piria, Annalen, 1851, 78, 31); iron filings and acetic acid (Béchamp. Ann. Chim. Phys. 1854, [iii.] 42, 195; Balló, Ber. 1870, 3, 288, 673); tin and hydrochloric acid (Roussin, Compt. rend. 1861, 52, 797); zinc and hydrochloric acid (Bottger, Dingl. poly. J. 1870, 197, 458); alcoholic potash (Klobukowsky, Ber. 1877, 10, 571); zinc-dust and aqueous calcium chloride (Dechend, D. R.-P. 43230); or hydrogen and reduced copper at 330°–350° (Sabatier and Senderens, Compt. rend. 1902, 135, 225).[1]

It is also obtained when α-naphthol is heated with ammonia under pressure at 150°–160° for 60–70 hours (Badische, D. R.-P. 14612). The yield may reach 70 p.c. of that calculated if the naphthol be heated with ammonia-calcium chloride at 270° for 8 hours, but dinaphthylamine is also formed in quantities varying with the conditions employed (Benz, Ber. 1883, 16, 14). Substitution of acetamide at 270° for ammonia gives a 50 p.c. yield of acetyl-α-naphthylamine, together with about 15 p.c. of dinaphthylamine (Calm, Ber. 1882, 15, 615), but replacement of ammonia by sodamide at 220°

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[1] This process has not yet been developed for nitronaphthalene, although applicable to nitrobenzene (*v.* art. ANILINE).

leads to the production of 1-*amino-5-naphthol* (Sachs, D. R.-P. 181333).

Preparation.—On the large scale α-naphthylamine is prepared by reducing granulated α-nitronaphthalene (15 pts.) with soft iron borings or 'swarf' (20 pts.), hydrochloric acid (1 pt.),[1] and water (10 pts.) at 50°–70° in an apparatus similar to that used in the manufacture of aniline, but provided with a wide exit-pipe for the escaping gases instead of a condenser. For complete reduction, stirring for 6-8 hours after the introduction of the nitronaphthalene is required. To remove the acid, milk of lime is added to the product, and the naphthylamine separated by distillation either in a vacuum or by the aid of superheated steam, the vapour being driven into the condenser as rapidly as possible. The yield amounts to about 70 p.c. of that calculated.[2] The crude base is purified by a second distillation, but always contains appreciable quantities of naphthalene, owing to decomposition during the first distillation (Witt, Chem. Ind. 1887, 10, 218; Paul, Z. angew. Chem. 1897, 10, 145), and of β-naphthylamine, the origin of which is obscure (*v.* β-nitronaphthalene). From β-naphthylamine it may be freed either by repeated crystallisation from warm light petroleum, in which the β-base is the more soluble (Erdmann, Annalen, 1893, 275, 217, footnote), or by warming it with 10 p.c. of its weight of xylene, allowing the homogeneous mixture to cool and solidify, breaking up the solid mass and separating the pure crystalline α-base in a centrifuge (Weiler-ter-Meer, D. R.-P. 205076; Eng. P. 16446 of 1907). The residue left after evaporation of the mother liquor to dryness contains both bases: if it is dissolved in hot dilute hydrochloric acid, most of the α-base separates as the crystalline hydrochloride on cooling, while from the filtrate the β-base is precipitated as sulphate by the addition of dilute sulphuric acid (Weiler-ter-Meer, *l.c.*; *cf.* Reverdin and Noelting, Sur la constitution de la Naphtaline, ed. 1885, 35)

Identification.—α-Naphthylamine crystallises from most solvents in colourless scales or flat needles, melts at 50°, boils at 300° (Zinin, *l.c.*), and is but little volatile with steam. It is easily soluble in alcohol, ether, or aniline, but almost insoluble in water, of which 100 c.c. dissolve only about 0·167 gram at the ordinary temperature (Balló, *l.c.*). On exposure to the air, the technical product changes colour gradually to greyish-violet, owing possibly to the presence of a small quantity of 1:8-diaminonaphthalene (Witt, *l.c.*). Its odour is characteristic and unpleasant.

The salts are for the most part sparingly soluble in water. The *hydrochloride* B·HCl and the *sulphate* $B_2 \cdot H_2SO_4 + 2H_2O$ form scales; the *platinichloride* $(B \cdot HCl)_2PtCl_4$ is a crystalline powder. The *picrate*, B·HA, forms sparingly soluble prisms, m.p. 161° (Smolka, Monatsh. 1885, 6, 923; *cf.* Suida, Ber. 1908, 41, 1913).

Reactions.—Diazotised, it forms the first component of many *azo*-dyes. It also couples with diazotised bases forming the middle or end component of *disazo*-dyes. From its *diazo*-compound, α-*naphthol* can be obtained, and is also formed when α-naphthylamine hydrochloride or sulphate is digested with water at 200°. By sulphonation it furnishes a series of *mono-*, *di-* and *tri-sulphonic acids*. Reduction in boiling amyl alcoholic solution with sodium converts it into ar.-*tetrahydro-α-naphthylamine*. When heated with zinc chloride or calcium chloride at 280° it undergoes partial decomposition into *αα′-dinaphthylamine* and ammonia (Benz, *l.c.*).

Oxidised by potassium dichromate and dilute sulphuric acid it yields 1:4-[α-]*naphthaquinone* and *phthalic acid* (Monnet, Reverdin and Noelting, Ber. 1879, 12, 2306), but with oxidising agents such as ferric chloride, silver nitrate, mercuric chloride, or chromic acid, its salts in aqueous solution produce an azure-blue precipitate of *naphthamein*, which rapidly becomes purple, dissolves in chloroform, and is not bleached by sulphurous acid (Piria, Annalen, 1851, 78, 64; Schiff, *ibid.* 1857, 101, 92; 1864, 129, 255).

Commercial tests.—Commercial α-naphthylamine should have the right melting-point and dissolve almost completely in dilute acids. The proportion of naphthalene present can be determined by distilling the sample with excess of hydrochloric acid in a current of steam and extracting the distillate with ether.

Acyl Derivatives

Formyl-α-naphthylamine, obtained by boiling α-naphthylamine with 16·3 p.c. formic acid (6·2 pts.) for half an hour, crystallises from water in needles, m.p. 138·5° (Tobias, Ber. 1882, 15, 2447).

Acetyl-α-naphthylamine (*acet-α-naphthalide*) is formed by heating α-naphthol with ammonium acetate at 270°–280° (Calm, Ber. 1882, 15, 615), and prepared by boiling α-naphthylamine with 1·25 times its weight of glacial acetic acid for 4–5 days (Liebermann and Dittler, Annalen, 1876, 183, 229). It crystallises in needles, m.p. 159°, is easily soluble in alcohol and acetic acid, and dissolves moderately in hot but is almost insoluble in cold water (Liebermann and Dittler, *l.c.*; Tommasi, Bull. Soc. chim. 1873, [ii.] 20, 20).

Reactions.—Nitration converts it into a mixture of 2-*nitro-* and 4-*nitro-acetyl-α-naphthylamine* and finally into 2:4-*dinitroacetyl-α-naphthylamine*. By sulphonation with warm 20-25 p.c. anhydro-acid it yields chiefly *acetyl-α-naphthylamine-5-sulphonic acid*, the 4-*sulphonic acid* being the minor product, but with 35 p.c. anhydro-acid below 30° the 5:7-*disulphonic acid*

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[1] Various explanations have been given of the process of reduction in which water, iron, and relatively very small quantities of hydrochloric acid are used (*cf.* Witt, *l.c.*; Wohl, Ber. 1894, 27, 1436; Raikow, Z. angew. Chem. 1916, 29, i. 197). According to Raikow, the 'activating' influence of salts of heavy metals on the interaction of metals with water is the underlying principle of this mode of reduction:—

$$3Fe + 6HCl + C_{10}H_7 \cdot NO_2 \rightarrow 3FeCl_2 + 2H_2O + C_{10}H_7 \cdot NH_2$$

$$3FeCl_2 + 3H_2O \rightarrow [3Fe(OH)_2 + 6HCl] + 3Fe + C_{10}H_7 \cdot NO_2$$

$$\rightarrow 3Fe(OH)_2 + 3FeCl_2 + 2H_2O + C_{10}H_7 \cdot NH_2$$

The hydrolytic decomposition of the ferrous chloride brings a further quantity of iron into solution and an equivalent quantity of ferrous chloride is regenerated.

[2] Other processes for the recovery of the base have been devised in which either the iron and iron oxide are removed electromagnetically from the reduction product fused at 50°–60° (Landshoff, D. R.-P. 83560), or the reduction product is extracted by a relatively small quantity of a solvent, such as benzene (Landshoff, D. R.-P. 184497).

is obtained.[1] In acetic acid solution with chlorine it gives *acetyl-2 : 4-dichloro-α-naphthylamine* (Cleve, Ber. 1887, 20, 448), but with sodium chlorate and hydrochloric acid *acetyl-4-chloro-α-naphthylamine* (Reverdin and Crépieux, Ber. 1900, 33, 682).

Alkyl Derivatives.

Methyl-α-naphthylamine, obtained by boiling a solution of formyl-α-naphthylamine in xylene with sodium (1 at.), adding methyl iodide (1 mol.) and saponifying the methyl derivative by dilute sulphuric acid, is an oil, b.p. 293° (Fischer, Annalen, 1895, 286, 159; *cf.* Landshoff, Ber. 1878, 11, 638).

Reactions.—It has been used as end component in certain *disazo*-dyes (*cf.* Cassella, D. R.-P 71329). The 4-*sulphonic acid* can be prepared from α-naphthol-4-sulphonic acid by interaction with methylamine and methylamine bisulphite at 150° (Badische, D. R.-P. 121683; Eng. P. 18726 of 1900).

Dimethyl-α-naphthylamine, obtained by heating α-naphthylamine hydrochloride with methyl alcohol (2 mols.) during 6-8 hours under pressure at 170°, is an oil, b.p. 272°–274°, sp gr. 1·0423 at 20° (Friedlander and Welmans, Ber. 1888, 21, 3124; *cf.* Pinnow, Ber. 1899, 32, 1406). Its *chloro-*, *nitro-* and *nitroso-* derivatives have been described; the hydrochloride of the *nitroso-* derivative decomposes into *nitroso-α-naphthol* and dimethylamine in aqueous or alcoholic solution.

Reactions.—By sulphonation with 95 p.c sulphuric acid at 130° it furnishes *dimethyl-α-naphthylamine-5 sulphonic acid*,[2] $HA+H_2O$, sparingly soluble scales, together with an easily soluble isomeride (Fussganger, Ber. 1902, 35, 977; *cf.* Friedlander and Welmans, *l.c.*). Reduction in boiling amyl alcohol solution by sodium converts it into ar.-*tetrahydrodimethyl-α-naphthylamine*.

Ethyl-α-naphthylamine is an oil, b.p. 303° under 722·5 mm. (Friedlander and Welmans, *l.c.*), 325°–330° under 776 mm. and 191° under 16 mm. (Morgan and Micklethwait, Chem. Soc. Trans. 1907, 91, 1516), which, on reduction in boiling amyl alcohol solution with sodium, furnishes ar-*tetrahydroethyl-α-naphthylamine*.

Diethyl-α-naphthylamine, obtained by heating α-naphthylamine with caustic soda (2 mols) a little water and ethyl bromide or iodide (2 mols.) at 110°–120°, and separated easily from the quaternary compound, m.p. 98°–100°, also formed, is an oil, b.p. 283°–285°, sp.gr. 1·005 (Friedlander and Welmans, *l c.*).

Aryl Derivatives.

Phenyl-α-naphthylamine, obtained by heating α-naphthylamine with aniline hydrochloride at 280° for 36 hours (Girard and Vogt, Bull. Soc. chim. 1872, [ii.] 18, 68; Streiff, Annalen, 1881, 209, 152), is more conveniently prepared by heating α-naphthol (1 mol.) with aniline (2 mols.) and anhydrous calcium chloride (1 mol.) in an autoclave for 10 hours at 280°–300° (Friedlander, Ber. 1883, 16, 2077; *cf.* Katayama, J. Soc. Chem. Ind. 1917, 36, 865). A yield of 85 p.c. is said to be obtained when α-naphthylamine is heated with aniline (1 mol.) and 0·5 p.c. of iodine at 230°–250° for 8 hours (Knoll, D. R.-P. 241853; Knoevenagel, J. pr. Chem. 1914, [ii.] 89, 20). It crystallises in prisms, m.p. 62°, b.p. 335° under 258 mm. or 226° under 15 mm., is insoluble in dilute acids, and couples with diazotised bases as end component in *disazo-* dyes (*cf.* Bayer, D. R.-P. 48924; Eng. P. 14442 of 1888).

o-Tolyl-α-naphthylamine, obtained by using *o*-toluidine instead of aniline in the foregoing methods, forms needles, m.p. 94°–95°, b.p. 198°–202° under 9 mm. (Friedlander, *l.c.*; Knoll, *l c*).

p-Tolyl-α-naphthylamine, also obtained similarly by the use of *p*-toluidine in place of aniline, forms prisms, m.p. 78°–79°, b.p. 360° under 258 mm., or 236° under 15 mm. (Girard and Vogt, *l.c.*; Friedlander, *l c.*; Knoll, *l c.*). It couples with diazotised bases as end component in *disazo*-dyes (*cf.* Bayer, D. R.-P. 49808; Eng P. 14442 of 1888)

Aryl-α-naphthylaminesulphonic acids. Of these derivatives, the *phenyl-* (o- or p-*tolyl-*) 3-, 4-, 5-, 6-, 7-, and 8-*sulphonic acids* have been prepared by heating the corresponding α-naphthylaminesulphonic acids with aniline (*o-* or *p*-toluidine) and its hydrochloride at 160°–170°. The acids are very sparingly soluble in water; the sodium salts crystallise in scales, and, with the exception of the 3-, 7-, and 8-sulphonates, are sparingly soluble (Bayer, D. R.-P. 70349, 71158, 71168; Eng. P. 7337A of 1892).

Among the α-naphthylamine-di- and tri-sulphonic acids, arylation has been confined for the most part to those which contain one of the SO_3H groups in the same nucleus as and in either the 3- or the 4- position relatively to the NH_2 group. With these acids:—

(*a*) if the SO_3H group be present in the 4-position, it is exchanged for hydrogen. Thus the α-naphthylamine- 4 : 6-, 4 : 7-, and 4 : 8-disulphonic acids by arylation furnish respectively the *phenyl-* (o- or p-*tolyl-*)*α-naphthylamine*-6-, 7-, and 8-*monosulphonic acids* (Aktienges., D. R.-P. 158923; 159353; Eng. P. 15624, 24669 of 1904).

(*b*) if the SO_3H group be present in the 3-position, it is exchanged for an arylated NH_2 group. Thus the α-naphthylamine-3 : 6-, 3 : 7-, and 3 : 8- disulphonic acids by arylation yield respectively the *diphenyl-*(*di*-o- or *di*-p-*tolyl*)-1 : 3-*diaminonaphthalene*-6-, 7-, and 8-*monosulphonic acids* (Bayer, D. R.-P. 75296, 76414; Eng. P. 8898 of 1893).

α-NAPHTHYLAMINESULPHONIC ACIDS.

Introductory. — α - Naphthylaminesulphonic acids can be prepared by the following general methods, of which the last two are technically unimportant:

(1) By sulphonation of α-naphthylamine.

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[1] *Acetyl-α-naphthylamine*-2-, 4-, 5-, 6-, 7-, and 8-*sulphonic acids*, and 3 . 6-, 4 . 6-, and 4 : 7-*disulphonic acids* can be prepared by heating solutions of the sodium salts of the respective α-naphthylaminesulphonic acids at 50°–60° with acetic anhydride for a few minutes (Hochst, D. R.-P. 129000; Eng. P. 17366 of 1898; *cf.* Nietzki and Zubelen, Ber. 1889, 22, 451; Cassella, D. R.-P. 74177; Eng. P. 15441 of 1893). Both acids and salts are very soluble in water, and each acid can be de-acetylated by boiling it with water.

[2] *Methyl-α-naphthylamine*-4- and 5-*sulphonic acids* and *dimethyl-α-naphthylamine*-4-, 5-, 7-, and 8-*sulphonic acids*, prepared by methylating the corresponding α-naphthylaminesulphonic acids, have been described (Fussgänger, *l.c.*).

(2) By nitration of naphthalenesulphonic acids and subsequent reduction.

(3) By sulphonation of α-naphthylamine-sulphonic acids obtained from nitronaphthalene-sulphonic acids.

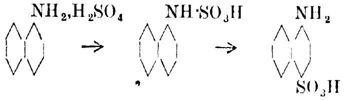
(4) By heating α-naphtholsulphonic acids, other than those which contain sulphonic groups in the 2- or 3- position, with ammonium sulphite solution and ammonia at 100°-150°, and afterwards acidifying the products (v. p. 416).

(5) By heating α-chloronaphthalenesulphonic acids with ammonia under pressure.

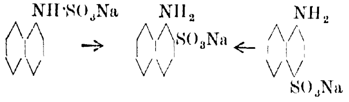
(6) By partial hydrolysis of α-naphthylamine-di- or tri-sulphonic acids.

Two of the monosulphonic acids are obtained by methods applicable only to them:

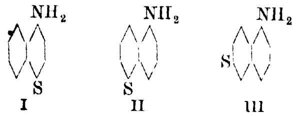
(a) α-Naphthylamine-4-sulphonic acid, one of the three monosulphonic acids formed from α-naphthylamine by sulphonation, is obtained mixed only with a small amount of the 5-sulphonic acid by 'baking' the acid sulphate of α-naphthylamine at 180°-200°:



(b) α-Naphthylamine-2-sulphonic acid is the only monosulphonic acid formed when sodium α-naphthylsulphamate or sodium α-naphthylamine-4-sulphonate is heated at about 200°:



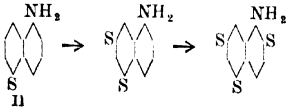
The *first general method*, the sulphonation of α-naphthylamine, leads to the formation of three mono-, three di-, and three tri-sulphonic acids. The composition of the sulphonation product depends on the four factors, concentration and relative quantity of the sulphuric acid, and temperature and duration of the reaction; but Erdmann has shown that it is possible to obtain, as chief product, successively the 4-, 5-, and 6-monosulphonic acid by prolonging the reaction without altering the temperature or the concentration of the sulphuric acid (Annalen, 1893, 275, 192; v. p. 413):

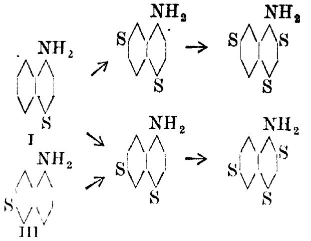


From the scheme which indicates the constitution of the products obtained by sulphonating each of these three acids it will be seen—

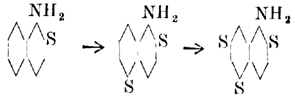
(i.) that the 2- position is not occupied in acids I, II, and III until trisulphonation occurs:

(ii.) that entry of the sulphonic group into the 3- or the 8- position does not take place:

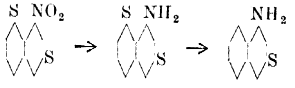




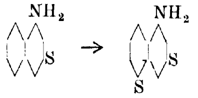
Although in the sulphonation of naphthylamine, its entry into the molecule is delayed until trisulphonation occurs, yet if introduced early (*v. supra*) the 2-sulphonic group is retained in position when α-naphthylamine-2-sulphonic acid interacts with sulphuric acid



The *second* and *third general methods* afford a means whereby several of the more important acids, those containing a sulphonic group in the 8- or *peri-* position, can be obtained. For the production of such acids, nitronaphthalene-sulphonic acids of corresponding constitution are reduced in weak acetic acid solution by iron, and in turn these acids by sulphonation or desulphonation may furnish α-naphthylamine-sulphonic acids not obtainable in other ways. Thus the 3-sulphonic acid, like the 3 · 8-disulphonic acid, arises from α-nitronaphthalene-3 : 8-disulphonic acid



and can be further sulphonated

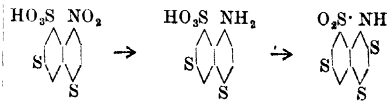


The limit of sulphonation is reached for most of the α-naphthylaminesulphonic acids when trisulphonation has been effected. Two exceptions only have been observed to this rule and in each the trisulphonic acid which undergoes further sulphonation:

(a) is prepared, not from α-naphthylamine, but by reduction of the corresponding α-nitronaphthalene-3 : 6 : 8- or 4 : 6 : 8-trisulphonic acid, and

(b) contains one SO_3H group in the *peri-* or 8- position relatively to the NH_2 radicle.

The tetrasulphonation product from either source is isolated from the sulphonation melt as a naphthasultamtrisulphonic acid:



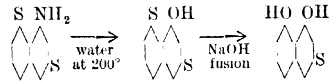
owing to the formation of the *peri*-anhydride or sultam, dehydration in the *peri*- position being a property which characterises both tri- and tetra-sulphonic acids of this type.

From solutions of the alkali monosulphonates the acids are precipitated, but from those of the di- and tri-sulphonates, acid salts separate on the addition of a mineral acid. A comparison of the relative strengths of the monosulphonic acids shows that the 2-acid is about 10 times as strong as the 4-, 5-, 6-, or 7-acid, and about 2000 times as strong as the 8-acid (Erdmann, Annalen, 1893, 275, 276).

A volumetric method for estimating *a*- (or *β*-) naphthylaminesulphonic acids, based on their different capacity for absorbing bromine has been devised by Vaubel (Chem. Zeit. 1893, 17, 1265). Most of these acids can be estimated accurately by titration with diazotised *p*-nitraniline (Bucherer, *cf.* J. Soc. Chem. Ind. 1907, 26, 818).

a-Naphthylaminesulphonic acids are used for the following purposes:—

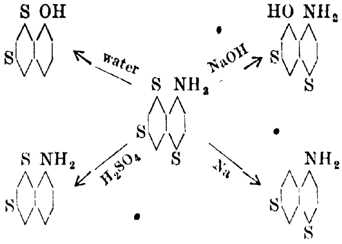
Conversion into a-naphtholsulphonic acids—The exchange of NH_2 for OH is effected not only by the diazo- reaction or by the bisulphite method (*v.* p. 416), but in certain cases by heating the acids with water at 180°–200° under pressure. This reaction takes place most readily when sulphonic groups are present in the same nucleus as, or in the 8- position relatively to, the amino- group, and, as the example shows, the amino- group is replaced more readily than the *a*-sulphonic group by hydroxyl.



Conversion into a-aminonaphtholsulphonic acids.—The exchange of SO_3H for OH is achieved either by digestion of the sulphonic acid with concentrated caustic soda solution at 180°–250° under pressure or by fusion with caustic soda at 180°–250°. As is customary, sulphonic groups in *a*- are more easily replaced than those in *β*- positions, and of groups in *a*- positions, when there is a choice, that in the 8- position is the first to be exchanged. Acids containing a 3-sulphonic group are decomposed by caustic soda at high temperatures furnishing hydroxy-toluic acids.

Conversion into a-naphthylaminesulphonic acids containing a smaller number of sulphonic groups.—The exchange of SO_3H for H is accomplished by the aid of sodium amalgam in the cold, or of zinc-dust in boiling dilute caustic soda solution, or of boiling 75 p.c. sulphuric acid. Groups in *a*- positions are the first to be eliminated. While the 8-sulphonic group is removed most readily by the first two of these desulphonating agents, hydrolysis by means of sulphuric acid leads preferentially to the elimination of the 4-sulphonic group.

The reactions summarised in the three preceding paragraphs may be illustrated in the case of *a*-naphthylamine-4 : 6 : 8-trisulphonic acid:—



It may be noted that the *a*-naphthylamine-4 : 6-, 4 : 7-, and 4 : 8-disulphonic acids, when heated with aniline or *p*-toluidine at 180°, furnish aryl-*a*-naphthylaminemonosulphonic acids by elimination of the 4-sulphonic group.

Conversion into diaminonaphthalenesulphonic acids.—The exchange of SO_3H for NH_2 takes place only when the acid contains a 3-sulphonic group, the 1 : 3-diaminonaphthalene derivative being produced by interaction of the acid with ammonia at 180°. Aniline and *p*-toluidine furnish 1 : 3-diaryl derivatives under these conditions.

Production of azo-dyes.—Diazotisation of the sulphonic acids proceeds normally, except in the case of *a*-naphthylamine-2-sulphonic acids which, as already indicated, yield diazo-oxides by exchange of the 2 sulphonic group for OH in the absence of mineral acid (*v.* p. 418).

Azo-dyes of two types, *para*- and *ortho*-, can be obtained from *a*-naphthylaminesulphonic acids of appropriate constitution by coupling with diazotised bases. When the *para*- position is occupied only by hydrogen *para*-azo-dyes are formed, except in the case of the 3- and 5-monosulphonic acids, when *ortho*-azo-dyes may also be obtained (Gattermann and Schulze, Ber. 1897, 30, 50; Gattermann and Liebermann, Annalen, 1912, 393, 198; *v.* p. 417).

Formation of carbamides.—Carbamides are formed from the 3 : 6- and 4 : 6-di- and 3 : 6 : 8- and 4 : 6 : 8-tri-sulphonic acids by interaction with nitroarylacyl chlorides (1 or 2 mols.), reduction and condensation with phosgene,

$$2X{\cdot}NH_2 \rightarrow 2X{\cdot}NH{\cdot}CO{\cdot}R{\cdot}NO_2$$
$$\rightarrow 2X{\cdot}NH{\cdot}CO{\cdot}R{\cdot}NH_2 \rightarrow [X{\cdot}NH{\cdot}CO{\cdot}R{\cdot}NH]_2CO$$

(where $X{\cdot}NH_2$ is the naphthylaminesulphonic acid and $NO_2{\cdot}R{\cdot}CO{\cdot}Cl$ is *m*-nitrobenzoyl or other nitroarylacyl chloride), which are said to be used in the production of dyestuffs and for the destruction of animal parasites (Bayer, D. R.-P. 288273, 289107, 289270, 289272).

a-NAPHTHYLAMINEMONOSULPHONIC ACIDS.[1]

(i.) *a*-**Naphthylamine-2-sulphonic acid** is obtained by heating sodium *a*-naphthylamine-4-sulphonate (naphthionate) at 200°–250°, but owing to the imperfect distribution of heat throughout the mass, the yield does not exceed 50 p.c (Landshoff, D. R.-P. 56563; Eng. P. 6195 of 1890; *cf.* Erdmann, Annalen, 1893, 275, 225). If, however, the naphthionate, suspended in boiling naphthalene, be heated at 180°–230° for 2–3 hours, and the naphthalene afterwards removed by distillation with steam, the yield is almost quantitative, and the product contains as impurity only a small quantity of α-naphthylamine (Bayer, D. R.-P 72833). This acid is also formed when α-naphthylamine is heated with sulphanilic acid or its homologues at 180°–250° (Bayer, D. R.-P. 75319); or with α-naphthylamine-4- or β-naphthylamine-8-sulphonic acid at 160°–230° (Bayer, D. R.-P. 77118; Eng. P. 21139 of 1892); or when α-naphthylsulphamic acid is heated at 170°–240° (Tobias, D. R.-P. 79132; Eng P. 15067 of 1894).

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[1] In every case where the constitution of an *a*-naphthylaminesulphonic acid is given, the NH_2 group is supposed to be in the position '1.'

Identification.—The *acid* crystallises in needles, soluble in 244 parts of water at 20°, or in 31·3 parts at 100° (Dolińska, Ber 1905, 38, 1836). The *barium* BaA_2+H_2O and *calcium* CaA_2 salts form sparingly soluble scales; the *potassium* salt KA, needles sparingly soluble in cold water; the *sodium* salt NaA, scales soluble in 10 parts of boiling or 60 parts of cold water. It is convertible into *α-chloronaphthalene-2-sulphonyl chloride*, needles, m p. 80°, and *1:2-dichloronaphthalene* (Cleve, Ber. 1891, 24, 3472).

Reactions.—From its sparingly soluble *diazo*-compound, *α-naphthol-2-sulphonic acid* has been obtained. Nitration converts it into *5 nitro-α-naphthylamine-2-sulphonic acid.* On sulphonation with 10 p.c. anhydro-acid in the cold it yields *α-naphthylamine-2:5-disulphonic acid.*

(ii.) α - **Naphthylamine - 3 - sulphonic acid** (*Cleve's* [γ-]*acid*) can be obtained by the reduction of α-nitronaphthalene-3-sulphonic acid with ferrous sulphate (Cleve, Ber 1886, 19, 2181). It is also formed when sodium α-naphthylamine-3:8-disulphonate is boiled with 75 p.c. sulphuric acid (Kalle, D. R.-P. 64979), or with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934), or is reduced either by sodium amalgam in the cold (Friedlander and Lucht, Ber. 1893, 26, 3032; Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911) or electrolytically (Bayer, D. R.-P. 248527; 251099; Eng. P. 28173 of 1911).

Identification.—The *acid* forms sparingly soluble needles; the *barium* salt BaA_2+H_2O forms scales and, like the *calcium*, *potassium* and *sodium* NaA salts, is very soluble in water (Cleve, Ber 1888, 21, 3271). It is convertible into *α-chloronaphthalene-3-sulphonyl chloride*, prisms, m.p. 106°, and *1:3-dichloronaphthalene* (Cleve, *l c.*; Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 240).

Reactions.—It couples with diazotised bases[1] as the middle component of *disazo*-dyes, but has been little used for this purpose. From its *diazo*-compound *α-naphthol-3-sulphonic acid* has been obtained. Fusion with caustic alkali at 250°–260° gives *1-amino-3-naphthol.* Digestion with 60 p.c. caustic soda solution at 250°–280° furnishes o-*toluic acid* (Kalle, D. R.-P. 79028), but with ammonia at 180° gives *1:3-diaminonaphthalene* or with aniline at 170° *diphenyl-1:3-diaminonaphthalene.* By sulphonation with 20 p.c. anhydro-acid in the cold, it yields *α-naphthylamine-3:5-disulphonic acid.*

(iii.) α-**Naphthylamine - 4 - sulphonic acid** (*naphthionic acid*), mixed with α-naphthylsulphamic acid, was first obtained by boiling α-nitronaphthalene with ammonium sulphite in alcoholic solution (Piria, Annalen, 1851, 78, 31). It is formed together with the more soluble 5-sulphonic acid, when α-naphthylamine is sulphonated with 'fuming' sulphuric acid (*cf.* Erdmann, Annalen, 1888, 247, 315), and constitutes the sole product when it is heated with 4–5 times its weight of sulphuric acid at 100°–120°, or with 3 times its weight of sulphuric acid at 130° until the product is soluble in alkali (Witt, Ber. 1886, 19, 57, 578; *cf.* Verein, Eng. P. 2237 of 1883). Mixed with a small amount (3–5 p.c.) of the 5-sulphonic acid and some unchanged α-naphthylamine, it is obtained by 'baking' acid α-naphthylamine sulphate, or a mixture of α-naphthylamine and sulphuric acid in the proportion to form this salt, at 180°–200° preferably in a vacuum (Nevile and Winther, Chem. Soc. Trans. 1880, 37, 632; Verein, *l.c.*; Paul, Z. angew. Chem. 1896, 9, 685), *or* by heating α-naphthylamine with 3 times its weight of potassium bisulphate at 200° (Bischoff and Brodsky, Ber. 1890, 23, 1914). It is also formed from α-naphthylamine-4:8-disulphonic acid by reduction with zinc-dust and boiling dilute caustic soda solution (Kalle, D. R.-P. 233934), or with sodium amalgam in the cold (Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911), or electrolytically (Bayer, D. R.-P. 248527, 251099; Eng. P. 28173 of 1911).

This acid also is the product when the bisulphite method is applied to sodium α-naphthol-4-sulphonate (Badische, D. R. P. 117471; Eng. P. 1387 of 1900; *cf.* p. 416); *or* when sodium α-chloronaphthalene-4-sulphonate is heated with 25 p.c. ammonia solution at 200°–210° (Oehler, D. R.-P. 72336).

Preparation.—Fused α-naphthylamine (50 kilos.) is stirred into sulphuric acid (36·5 kilos.) and the mixture heated at 170°–180° until a homogeneous mass is obtained. Crystallised oxalic acid (2·5 kilos.) is then stirred in, and the frothy mass, spread on leaden trays, is heated in an oven at 170°–180° during 8 hours. When cold, the porous, grey product is ground to a powder, extracted by hot milk of lime, the filtrate precipitated by hydrochloric acid and the washed precipitate converted into sodium salt (64 kilos.). Should the salt still contain α-naphthylamine or the 5-sulphonate, the former may be extracted by solvent naphtha, and the latter removed by fractional crystallisation (*cf.* Schultz, Chem. d. Steinkohlenth., 3rd ed. i. 202).

Identification.—The *acid* $HA+\frac{1}{2}H_2O$ forms small lustrous needles, which dissolve in 3225 parts of water at 20°, or in 438 parts at 100° (Doliński, Ber. 1905, 38, 1836). The *barium* salt BaA_2+8H_2O in scales, *calcium* salt CaA_2+8H_2O in monoclinic tables, *potassium* salt KA in scales, and *sodium* salt $NaA+4H_2O$ in large monoclinic prisms, dissolve readily in water, and, like the acid, show marked blue fluorescence in dilute solution. It is convertible into *α-chloronaphthalene-4-sulphonyl chloride*, triclinic prisms, m.p. 95°, and *1:4-dichloronaphthalene* (Cleve, Ber. 1887, 20, 73).

Reactions.—Diazotised, it forms the first component of many *azo*-dyes. It couples with diazotised bases, forming ortho-*azo*-dyes, but is valueless as a middle component, owing to the amino- group, when in the *ortho*- position relatively to the diazo- complex, being difficult to diazotise.

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[1] Diazobenzene chloride is an exception (*cf.* Gattermann and Schulze, Ber. 1897, 30, 54). With diazotised *p*-nitraniline coupling takes place in the *ortho*- position (Gattermann and Liebermann, Annalen, 1912, 393, 200).

From its sparingly soluble, microcrystalline, yellow *diazo-* compound, *α-naphthol-4-sulphonic acid* may be obtained. This acid is also the product when the sodium salt is digested either with sodium bisulphite solution at 85°-90°, followed by acidification, or with 50 p.c. caustic soda solution at 240°-260°. With sodium amalgam in the cold it gives *α-naphthylamine*. By sulphonation with 25 p.c. anhydro-acid below 30°, it is converted into a mixture of *α-naphthylamine-4:6-* and *4:7-disulphonic acids*. Prolonged heating with sulphuric acid at 130° converts it successively into the *5-sulphonic acid* and the *6-sulphonic acid*, and it is the most easily hydrolysed acid of the three. Its sodium salt, when heated at 200°-250°, is converted into *sodium α-naphthylamine-2-sulphonate*.

Acetyl-α-naphthylamine-4-sulphonic acid, the minor product of the sulphonation of acetyl-α-naphthylamine with 20-25 p.c. anhydro-acid (Schultz, Ber. 1887, 20, 3161; cf. 5-sulphonic acid), is obtained as sodium salt by stirring acetic anhydride (7 pts.) into a solution of sodium α-naphthylamine-4-sulphonate (15 pts.) at 60°-70°, and salting out the product. Both the *acid* and the *sodium* salt are crystalline and readily soluble in water (Hochst, D. R.-P. 129000; Eng. P. 17366 of 1898; Nietzki and Zubelen, Ber. 1899, 22, 451). Nitration converts it into the *5-nitro*-derivative.

(iv.) α-**Naphthylamine-5-sulphonic acid** (*Laurent's acid*; *Cleve's [α-]naphthalidinesulphonic acid*)[1] is obtained by reduction of α-nitronaphthalene-5-sulphonic acid (Laurent, Compt. rend. 1850, 31, 538; *cf.* Cleve, Forhandl. 1875, 9, 13; Bull. Soc. chim. 1875, [ii.] 24, 511; Erdmann, Annalen, 1893, 275, 264; Schollkopf, D. R.-P. 40571; Eng. P. 15775 of 1885). It constitutes the chief with the 4-sulphonic acid as subsidiary product, when α-naphthylamine is warmed with twice its weight of 'fuming' sulphuric acid (Cleve, Forhandl. 1876, 7, 39; *cf.* Schmidt and Schaal, Ber. 1874, 7, 1367; Erdmann, Annalen, 1888, 247, 315); *or* when α-naphthylamine hydrochloride is sulphonated in the cold with 20-25 p.c. anhydro-acid (Witt, Ber. 1886, 19, 578; Schultz, Ber. 1887, 20, 3161; Mauzelius, *ibid.* 3403), *or* when acetyl-α-naphthylamine is sulphonated with 3-4 times its weight of 20-25 p.c. anhydro-acid and the product de-acetylated by boiling the melt with water (Lange, Ber. 1887, 20, 2940; Ewer and Pick, D. R.-P. 42874; Schultz, *l.c.*), but is the minor product obtained in the manufacture of the 8-sulphonic acid from naphthalene-α-sulphonic acid by nitration and reduction. It is also formed when sodium α-chloronaphthalene-5-sulphonate is heated with 25 p.c. ammonia solution at 200°-210° (Oehler, D. R.-P. 72336)

Preparation.—The product obtained by sulphonating α-nitronaphthalene at 90 with 10-20 p.c. anhydro-acid is poured on to an equal weight of ice, and the precipitated α-nitronaphthalene-5-sulphonic acid (*q.v.*) removed by filtration, mixed with water, reduced by iron, and converted into sodium salt in the usual way. Or the product of the sulphonation of α-naphthylamine hydrochloride with twice its weight of 20-25 p.c. anhydro-acid in the cold, is poured on to ice, the precipitated acid converted into calcium salt, and the less soluble calcium 5-sulphonate separated by fractional crystallisation from the small amount of 4-sulphonate always formed in this process.

Identification.—The *acid* crystallises in anhydrous needles, soluble in about 940 parts of cold water. The *barium* salt BaA_2+6H_2O, in aggregates of small scales; *calcium* salt CaA_2+9H_2O, in tables; *potassium* salt $KA+H_2O$, in needles; and *sodium* salt $NaA+H_2O$, in aggregates of needles, dissolve readily in water; both acid and salts show greenish fluorescence in dilute aqueous solution (Cleve, Bull. Soc. chim. 1875, [ii.] 24, 511; Witt, *l.c.*; Mauzelius, *l.c.*) It is convertible into *α-chloronaphthalene-5-sulphonyl chloride*, prisms, m.p. 95°, and *1:5-dichloronaphthalene* (Erdmann, Annalen, 1888, 247, 353).

Reactions.—Diazotised, it forms the first component of many *azo*-dyes. With diazotised *p*-nitraniline it couples, forming both the ortho- and the para *azo*-dye. From its sparingly soluble, yellow, crystalline *diazo-* compound, *α-naphthol-5-sulphonic acid* may be obtained. Digestion with concentrated caustic soda solution at 250° converts it into *1-amino-5-naphthol*. By sulphonation with 35 p.c. anhydro-acid at 90°-120°, it yields *α-naphthylamine-2:5:7-trisulphonic acid*, the intermediate *5:7-disulphonic acid* being obtained by sulphonation of its acetyl derivative with 30 p.c. anhydro-acid in the cold, and subsequent de-acetylation.

(v.) α-**Naphthylamine-6-sulphonic acid** (*Cleve's [β-]acid*; *Erdmann's [μ-]acid*), formed when α-naphthylamine-4-sulphonic acid or 5-sulphonic acid is heated with sulphuric acid at 125°-130° for many hours (Erdmann, Annalen, 1893, 275, 200), is prepared by reduction of α-nitronaphthalene-6-sulphonic acid by ammonium sulphide or by iron and dilute sulphuric acid (Cleve, Ber. 1887, 20, 74).

Preparation.—The product obtained by nitrating naphthalene-β-sulphonic acid, which consists almost entirely of a mixture of the α-nitronaphthalene-6- and 7-sulphonic acids (*q.v.*), after dilution with water, is neutralised by lime and the filtrate, rendered acid by acetic acid in small quantity, reduced at the boiling-point by soft-iron borings. The resulting solution is then freed from iron by milk of lime, concentrated, and either treated with sodium carbonate to obtain the greater part of the 7-isomeride as sparingly soluble sodium salt, or the mixed Cleve acids precipitated from the concentrated solution by hydrochloric acid.

For many purposes, as for example the production of 1:4-diaminonaphthalene-6-sulphonic acid or numerous azo-dyes, a separation of the mixed Cleve acids is unnecessary. If the pure acids are required, then, according to Fierz, enough magnesite is added to the diluted nitration melt to combine with the calculated amount of sulphonic acid present, the excess of sulphuric acid neutralised by lime, and the reduction carried out as just described. When the boiling liquid has become colourless it is neutralised by the addition of magnesite, and the filtrate after concentration to a small bulk precipitated by hydrochloric acid. The precipitate, 2–3 days later, is collected on a filter (the filtrate being violet owing to the presence of hydroxylamine compounds) and washed with cold water until colourless. As much as 28 p.c. of the calculated yield of Cleve acids may be lost in this filtrate. The acids, now free from impurities, isomerides and disulphonic acids, are converted into sodium salts and finely powdered common salt stirred in the hot concentrated solution during one day, to effect a complete separation of the pure sodium 7-sulphonate. From the mother liquor on acidification, a precipitate of the 6-sulphonic acid in an almost pure state is obtained, the remaining impurity being removable by retreatment (Fierz-David, Dye Chemistry, p. 25).

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[1] The 'α-naphthylamine-[δ-]sulphonic acid' obtained by Hirsch by heating α-naphthylamine with 5 times its weight of sulphuric acid at 125°-130° for 8-9 hours (Hirsch, D. P. Anm. H. 7291; Ber. 1888, 21, 2370) is a mixture of the 5-sulphonic acid with some 6-sulphonic acid (Erdmann, Annalen, 1893, 275, 223).

Identification.—The *acid* $HA + 2H_2O$ forms needles soluble in 1000 parts of water at 16°. The *barium* salt $BaA_2 + H_2O$ in needles, is only sparingly, but the *calcium* salt $CaA_2 + 7H_2O$ in tablets, *potassium* salt $KA + H_2O$ in scales and *sodium* salt $NaA + 4\frac{1}{2}H_2O$ in thin tablets are easily soluble in water (Cleve, Forhandl. 1876, 7, 54; Bull. Soc. chim. 1876, [ii.] 26, 447; Erdmann, *l.c.* 265). It is convertible into *α-chloronaphthalene-6-sulphonyl chloride*, diamond shaped plates, m.p. 114°–115° (Cleve, Ber. *l.c.*), and 1 : 6-*dichloronaphthalene* (Erdmann, *l.c.*).

Reactions.—It couples with diazotised bases and is of importance as the middle or end component of *disazo-* or *trisazo-* dyes. From its *diazo-* compound or by the bisulphite method *α-naphthol-6-sulphonic acid* may be obtained. Fusion with caustic alkali converts it into 1-*amino*-6-*naphthol*. By sulphonation with 10 p.c. anhydro-acid it yields *α-naphthylamine-4 : 6-disulphonic acid*.

(vi.) α-**Naphthylamine-7-sulphonic acid** (*Cleve's* [*θ*-] or [*δ*-]*acid*; *Cleve's acid*) is obtained by the reduction of α-nitronaphthalene-7-sulphonic acid (Cleve, Ber. 1888, 21, 3264; Erdmann, Annalen, 1893, 275, 272), *or* by boiling α-naphthylamine-2 : 7-disulphonic acid with 80 p.c. sulphuric acid (Kalle, D. R.-P. 62634), *or* from α-naphthol-7-sulphonic acid by the bisulphite method (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; cf. p. 416).

Preparation.—This acid is obtained, mixed with about an equal amount of the 6-sulphonic acid (*q.v.*) by reduction of the nitration product of naphthalene-*β*-sulphonic acid and easily separated from its isomeride owing to the sparing solubility of its sodium salt in brine.

Identification.—The *acid* $HA + H_2O$ forms scales soluble in 220 parts of water at 25°. The *barium* salt BaA_2 in needles, is only sparingly, but the *calcium* salt $CaA_2 + 2H_2O$, *potassium* salt in scales, and *sodium* salt $NaA + \frac{1}{2}H_2O$ in needles are easily soluble in water (Cleve, *l.c.*). It is convertible into *α-chloronaphthalene-7-sulphonyl chloride*, elongated prisms, m.p. 94° (Cleve, Ber. 1892, 25, 2481), and 1 : 7-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 49).

Reactions.—It couples with diazotised bases, and is of much importance as the middle or end component of many *disazo-* and *trisazo-* dyes.[1] From its *diazo-* compound or by the bisulphite method, *α-naphthol-7-sulphonic acid* may be obtained. Digestion with 60 p.c. caustic soda solution at 250° converts it into 1-*amino*-7-*naphthol*. By sulphonation with 25 p.c. anhydro-acid at 50° it yields *α-naphthylamine-4 : 7-disulphonic acid*.

(vii.) α-**Naphthylamine-8-sulphonic acid** (*Schöllkopf acid*; S-*acid*; peri-*acid*) is obtained by reduction of α-nitronaphthalene-8-sulphonic acid in acid solution with iron (Schöllkopf, D. R.-P. 40571; Eng. P. 15775 of 1885); it is also formed when sodium 1 : 8-naphthasultam-2 : 4-disulphonate is digested with 20 p.c. hydrochloric acid at 150° (Dressel and Kothe, Ber. 1894, 27, 2140).

Preparation.—The product obtained by nitrating naphthalene-α-sulphonic acid, consisting almost entirely of a mixture of α-nitronaphthalene-5- and 8-sulphonic acids, after dilution with water is converted into calcium salt by means of lime and the filtrate rendered slightly acid by sulphuric acid, reduced by iron borings, precipitated by sodium carbonate and evaporated to a small bulk. Most of the sodium α-naphthylamine-8-sulphonate separates as a crystalline mass from the concentrated solution, and the remainder can be isolated from the highly soluble 5-sulphonate by further fractional crystallisation. The mother liquor, on acidification, furnishes the 5-sulphonic acid,[2] which can be purified by conversion into the sodium salt and repetition of the fractional crystallisation.

Identification.—The *acid* $HA + H_2O$ forms needles soluble in 4800 parts of water at 21° or in 238 parts of boiling water; the *potassium* salt KA scales, soluble in 280 parts of water at 19°, or in 67 parts at 100°, the *sodium* salt NaA scales or tables, soluble in 885 parts of water at 24°, or in 375 parts at 100° (Erdmann, Annalen, 1888, 247, 320). It is convertible into *α-chloronaphthalene-8-sulphonyl chloride*, scales, m.p. 101°, and 1 : 8-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 84).

Reactions.—It couples with diazotised bases, and has been used as middle or end component in *azo*-dyes. From its sparingly soluble *diazo*-compound, *naphthasultone* (the anhydride of α-naphthol-8-sulphonic acid) can be obtained. Digestion with water at 200° converts it into *α-naphthol-8-sulphonic acid*, and with 9 p.c. caustic soda solution at 220°–260° into 1 : 8-*dihydroxynaphthalene*, but fusion with caustic alkali at 200° furnishes 1-*amino*-8-*naphthol*. By dehydration with phosphorus oxychloride at 130°, it yields the anhydride *naphthasultam*, and with 40 p.c. anhydro-acid at 80°–90° *naphthasultam-2 : 4-disulphonic acid* is formed, but with 10 p.c. anhydro-acid in the cold sulphonation alone occurs, *α-naphthylamine-4 : 8-disulphonic acid* being the product.

Phenyl-α-naphthylamine-8-sulphonic

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[1] As this acid and the 6-isomeride, when equally pure, furnish dyes which are identical in strength and shade, the common experience that the 7-sulphonic acid gives the better yield must be referred to the greater readiness with which it can be purified (Fierz-David, Dye Chemistry, p. 26).

[2] Fierz, who describes the reduction and separation in greater detail, states that if the sulphonation product of naphthalene at low temperatures (containing therefore some naphthalene-β-sulphonic acid) be used instead of naphthalene-α-sulphonic acid for the nitration, the 5-sulphonic acid is nevertheless free from Cleve acids as the corresponding 6- and 7-nitro- acids are reduced only to hydroxylamine derivatives under the conditions employed and are lost (Helv. Chim. Acta, 1920, 3, 307; *cf.* Fierz-David, Dye Chemistry, p. 29).

acid is obtained when α-naphthylamine-8-sulphonic acid (1 pt.) is heated with aniline (3·5 pts.) and aniline hydrochloride (1 pt.) at 160°–170° for 10 hours, or with aniline (4 pts.) and benzoic acid (0·05 pt.) at 130°–140° for 8 hours (Bayer, D. R.-P. 70349, 71168; Eng. P. 7337A of 1892), *or* when, suspended in water, it is heated at 140° for 20 hours with aniline (3 pts.) dissolved in hydrochloric acid (Kalle, D. R.-P. 170630; Eng. P. 12326 of 1901), *or* when the acid sodium salt of α-naphthylamine-4 : 8-disulphonic acid (1 pt.) is heated with aniline (4 pts.) at 180° for 30 hours (Aktienges., D. R.-P. 158923; Eng. P. 15624 of 1904). The product, after being rendered alkaline, is freed from aniline by distillation with steam, and the phenylated acid precipitated by hydrochloric acid, or salted out. The *acid* is only sparingly, but the *sodium* salt easily soluble in water. It couples with diazotised bases forming *monoazo*-dyes.

α-NAPHTHYLAMINEDISULPHONIC ACIDS

(i.) α-**Naphthylamine-2 : 4-disulphonic acid** is obtained when α-naphthylamine-2 : 4 : 6-trisulphonic acid is reduced electrolytically or by sodium amalgam (Bayer, D. R.-P. 248527, 251099; 255724; Eng. P. 28172, 28173 of 1911) or, mixed with the 4-sulphonic acid in small amount, when α-nitronaphthalene is heated with sodium bisulphite solution at 100° (Hoechst, D. R.-P. 92082). Its *sodium* salt is easily soluble in water.

Reactions.—Its *diazo*- compound yields *naphthalene*-1 : 3-*disulphonic acid* by elimination of the amino- group, and 2 : 4-*dinitro-α-naphthol* when warmed with dilute nitric acid (Höchst, *l.c.*). Fused with caustic alkali, it furnishes 1-*amino-2-naphthol*-4 *sulphonic acid*, whilst its diazo- compound, oxidised by hypochlorite in sodium bicarbonate solution, furnishes the *diazo-oxide* of this acid (Badische, D. R.-P. 160536; Eng. P. 4997 of 1904).

(ii.) α-**Naphthylamine-2 : 5-disulphonic acid** is obtained from α-naphthylamine-2-sulphonic acid by sulphonation with 10 p.c. anhydro-acid in the cold (Landshoff, D. R.-P. 56563; Eng. P. 6195 of 1890). It is easily soluble, but its acid salts are only very sparingly soluble in water.

Reactions.—It yields *naphthalene*-1 : 6-*disulphonic acid* by elimination of the amino- group, and α-*naphthylamine*-5-*sulphonic acid* by partial hydrolysis with dilute sulphuric acid at 160° (Tobias, Ber. 1890, 23, 1631; Landshoff, *l.c.*). Digestion with 50 p.c. caustic soda solution at 240°–270° furnishes 1-*amino*-5-*naphthol*-2-*sulphonic acid*. By sulphonation with 40 p.c. anhydro-acid at 120° it is converted into α-*naphthylamine*-2 : 5 : 7-*trisulphonic acid*.

(iii.) α-**Naphthylamine-2 : 6-disulphonic acid**, stated to be obtained when α-naphthylamine-2 : 4 : 6-trisulphonic acid is heated with mineral acids, has not been described (Bayer, D. P. Anm. F. 31910).

(iv.) α-**Naphthylamine-2 : 7-disulphonic acid**, obtained by partial hydrolysis of α-naphthylamine-2 : 4 : 7-trisulphonic acid with water at 230° under pressure (Kalle, D. R.-P. 62634), is also formed when α-naphthylamine-2 : 5 : 7-trisulphonic acid is desulphonated either by sodium amalgam in the cold (Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911) or by boiling it with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934). It crystallises in needles; its *barium* salt is very sparingly soluble in water, and solutions of its alkali salts show bluish-green fluorescence (Kalle, D. R.-P. 62634).

Reactions.—It yields α-*naphthol*-2 : 7-*disulphonic acid* by the diazo- reaction, *naphthalene*-2 : 7-*disulphonic acid* by elimination of the amino- group, and α-*naphthylamine*-7-*sulphonic acid* by heating it with dilute sulphuric acid or water under pressure (Kalle, *l.c.*).

(v.) α-**Naphthylamine-2 : 8-disulphonic acid** is obtained from naphthasultam-2 : 4-disulphonic acid by partial hydrolysis with 40 p.c. sulphuric acid at 110° (Cassella, D. R.-P. 75710). It crystallises in moderately soluble long needles; the solutions of its alkali salts show green fluorescence.

Reactions.—With nitrous acid (1 mol.) it does not give a reactive diazo- compound, but it couples with diazotised bases forming *azo*-dyes. Fusion with caustic soda converts it into 1-*amino*-8-*naphthol*-2-*sulphonic acid*.

(vi.) α-**Naphthylamine-3 : 5-disulphonic acid** is the product formed by sulphonating α-naphthylamine-3-sulphonic acid with 4 times its weight of 20 p.c. anhydro-acid in the cold.

Identification.—The *acid potassium* salt, $KHA+2H_2O$, forms short needles convertible into α-*chloronaphthalene*-3 : 5-*disulphonyl chloride*, prisms, m.p. 130°, and 1 : 3 : 5-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 240).

(vii.) α-**Naphthylamine-3 : 6-disulphonic acid** (*Alén's* [α-]*acid*; *Freund's acid*) is obtained by reduction of α-nitronaphthalene-3 : 6-disulphonic acid (Alén, Förhandl. 1883, 8, 3; Freund, D. R.-P. 27346; Eng. P. 1069 of 1883 [1]; Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 82), *or* by boiling α-naphthylamine-3 : 6 : 8-trisulphonic acid with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934).

Preparation.—The nitration product of sodium naphthalene-2 : 7-disulphonate diluted with water is reduced by soft-iron borings, the iron and excess of sulphuric acid removed by lime, and the filtrate after precipitation by sodium carbonate acidified and evaporated to obtain the acid sodium salt.

Identification.—The *acid* forms needles, and, like the *barium* $BaA+4H_2O$ and *calcium* $CaA+5H_2O$ in tablets, also the *acid potassium* $KHA+3H_2O$ and *acid sodium* $NaHA+3H_2O$ salts in needles, is easily soluble in water (Alén, *l.c.*). It is convertible into α-*chloronaphthalene*-3 : 6-*disulphonyl chloride*, prisms, m.p. 114°, or needles, m.p. 127°, and 1 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—From its *diazo*- compound, α-*naphthol*-3 : 6-*disulphonic acid* can be obtained. This acid is also formed when it is digested with water at 180°, but when it is boiled with 75 p.c. caustic potash solution the product is a mixture of the 1-*amino*-3-*naphthol*-6-*sulphonic* and 1-*amino*-6-*naphthol*-3-*sulphonic acids*. Digestion with ammonia at 180° converts it into 1 : 3-*diaminonaphthalene*-6-*sulphonic acid*, and with aniline (or *p*-toluidine) at 150°–160° into

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[1] This acid, like the 3 : 7-acid, was regarded by Freund as a β-naphthylaminedisulphonic acid.

*diphenyl-(di-*p*-tolyl-)* 1 : 3-*diaminonaphthalene*-6-*sulphonic acid.*

Acylated by interaction with nitroacyl chlorides (1 or 2 mols.) such as *m*-nitrobenzoyl chloride or α-nitronaphthalene-5-sulphonyl chloride, followed by reduction of the nitro-groups and condensation of the resulting amino-derivatives with phosgene or carbon disulphide, it yields a series of *carbamide* or *thiocarbamide* derivatives (Bayer, D. R.-P. 288273; 289270; 289272).

(viii.) α-**Naphthylamine**-3 : 7-**disulphonic acid** (*Alén's* [β-]*acid*), prepared by reduction of α-nitronaphthalene-3 : 7-disulphonic acid (Freund, D. R.-P. 27346; Eng. P. 1069 of 1883; Cassella, D. R.-P. 57007, 58352; Levinstein, Eng. P. 2682 of 1891), is also formed when α-naphthylamine-3 : 5 : 7 trisulphonic acid is desulphonated either by sodium amalgam in the cold (Bayer, D. R.-P. 255721; Eng. P. 28172 of 1911) or by boiling it with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934)

Identification.—It is easily soluble in water, and, like its salts, shows blue fluorescence in solution. The *barium* salt $BaA+H_2O$, *calcium* salt $CaA+2H_2O$, and *acid potassium* salt KHA form sparingly soluble needles (Alén, Forhandl. 1883, 8, 26).

Reactions.—From its *diazo-* compound α-*naphthol*-3 : 7-*disulphonic acid* can be obtained. This acid is also formed when it is digested with water at 180°, but with 40 p.c. caustic soda solution at 200° the product is a mixture of 1-*amino*-7-*naphthol*-3-*sulphonic acid* with an isomeric acid (Cassella, D. R-P. 57007). Digestion with ammonia at 180° converts it into 1 : 3-*diaminonaphthalene*-7 *sulphonic acid*, and with aniline (or *p*-toluidine) at 150°–160° into *diphenyl* (*di*-p *tolyl*) 1 : 3-*diaminonaphthalene*-7-*sulphonic acid.*

(ix.) α-**Naphthylamine**-3 . 8-**disulphonic acid** ([ε-]*acid*) is obtained by reduction of α-nitronaphthalene-3 : 8-disulphonic acid in acid solution at the boiling-point by iron borings or on the small scale by zinc-dust (*cf.* Paul, Z. angew. Chem. 1896, 9, 562).

Preparation.—The mixture of this acid with α-nitronaphthalene-4 : 8-disulphonic acid, and some β-nitronaphthalenedisulphonic acids, obtained by nitrating a disulphonation melt containing the naphthalene-1 : 5- and 1 : 6-disulphonic acids, is diluted with water, neutralised by lime, acidified slightly by sulphuric acid, reduced hot by soft-iron borings, again neutralised by lime and the filtrate converted into sodium salt. After concentration of the filtrate to a small bulk, the 4 : 8-disulphonic acid separates from the solution in the course of several days as the normal sodium salt, the more soluble 3 : 8-salt being retained in the mother liquor from which it is precipitated as acid sodium salt by the addition of hydrochloric acid. The final mother liquor contains the highly soluble sodium β-naphthylaminedisulphonates (Aktienges., D. R.-P. 45776; Eng. P. 4625 of 1888; Ewer and Pick, D. R.-P. 52724; Bernthsen, Ber. 1889, 22, 3328; Schultz, Ber. 1890, 23, 77). The separation may be achieved in the same way with the barium salts but more rapidly as hot solutions may be used (S. Metro. Gas Co and Stanier, Brit. P. 161859).

Identification.—The *acid* H_2A+3H_2O forms very soluble scales The *barium* salt $BaA+4H_2O$ forms needles sparingly soluble, and the *acid barium* salt $BaH_2A_2+5H_2O$, microscopic needles almost insoluble in cold water; the *normal sodium* salt Na_2A+6H_2O very soluble, and the *acid sodium* salt $NaHA+2H_2O$ soluble in about 30 parts of cold water, crystallise in long needles or thin prisms (Bernthsen, *l.c.*). It is convertible into α-*chloronaphthalene*-3 : 8-*disulphonyl chloride*, needles, m.p. 110°, and 1 : 3 : 8-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 16)

Reactions.—It couples with diazotised *m*- or *p*-nitraniline (Aktienges., D. R.-P. 170513; 174548), but not with diazotised aniline (*cf.* Bayer, D. R.-P. 75084). From the *diazo-* compound, *naphthasultone*-3-*sulphonic acid*, but by prolonged boiling with dilute sulphuric acid α-*naphthol*-3 . 8-*disulphonic acid* is obtained. This disulphonic acid is also formed when α-naphthylamine-3 : 8-disulphonic acid is digested with water at 180°: desulphonation however occurs, α-*naphthylamine* 3-*sulphonic acid* being the product, when it is boiled with 75 p.c. sulphuric acid, or with zinc-dust and dilute caustic soda solution, or is acted on by sodium amalgam in the cold.

Fusion with caustic alkali below 210° furnishes 1-*amino*-8-*naphthol*-3-*sulphonic acid*, but when it is heated with 9 p.c. caustic soda solution at 250° it yields 1 : 8-*dihydroxynaphthalene*-3-*sulphonic acid.* Digestion with ammonia at 180° converts it into 1 . 3-*diaminonaphthalene*-8-*sulphonic acid* and with aniline (or *p*-toluidine) at 150°–160° into *diphenyl*-(*di*-p-*tolyl*-) 1 : 3-*diaminonaphthalene*-8-*sulphonic acid.* When sulphonated with 40 p.c. anhydro-acid at 80°–90°, *naphthasultamdisulphonic acid*-ε is the product.

(x.) α-**Naphthylamine**-4 : 6-**disulphonic acid** (*Dahl's* No. II. *acid* [1]) constitutes about 30 p.c. of the product obtained by sulphonating α-naphthylamine-4-sulphonic acid with 25 p.c. anhydro- acid in the cold (*v.* 4 : 7-disulphonic acid), and is separated by extraction of the mixed calcium salts with 85 p.c. alcohol in which it is soluble (Dahl, D. R.-P. 41597).

It is formed when α-naphthylamine-6-sulphonic acid is sulphonated with 10 p.c. (Cassella, D. P. Anm. C. 4021) or 25 p.c. anhydro-acid (Bayer, D. P. Anm. F. 7016; Eng. P. 15223 of 1893), or when α-naphthylamine-4 : 6 : 8-trisulphonic acid is boiled for some hours with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934), *or* when the bisulphite method is applied to α-naphthol-4 . 6-disulphonic acid (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Identification.—The *calcium* salt $CaA+5H_2O$ forms needles soluble in 85 p.c. but insoluble in 96 p.c. alcohol (Erdmann, Annalen, 1893, 275, 219), and, like the *potassium* and *sodium* salts, is very soluble in water; the *acid sodium* salt, in needles, is soluble in about 6 parts of water at 20° (Dahl, *l.c.*). It is convertible into α-*chloronaphthalene*-4 : 6-*disulphonyl chloride*, needles, m.p. 126°–127°, and 1 : 4 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

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[1] In Dahl & Co.'s patent (D. R.-P. 41597) an acid 'No. I' is described, the calcium salt of which is soluble in 96 p.c. alcohol. This acid, said to constitute 50 p.c. of the product when α-naphthylamine is heated with 4–5 parts of 25 p.c. anhydro-acid at 120°, could not be identified by Erdmann (Annalen, 1893, 275, 218), and is believed by him not to exist.

Reactions.—It couples with diazotised bases. From its moderately soluble *diazo-* compound or by the bisulphite method *α-naphthol*-4 : 6-*disulphonic acid* can be obtained. Fusion with caustic soda at 180°–200° converts it into 1-*amino*-6-*naphthol*-4-*sulphonic acid*, and at 200°–220° into 1 : 6-*dihydroxynaphthalene*-4-*sulphonic acid.* Heated with aniline (or *p*-toluidine) at 180°, it forms *phenyl-* (or p-*tolyl-*) *α-naphthylamine*-6-*sulphonic acid* by elimination of the 4-sulphonic group. By sulphonation with 35 p.c. anhydro-acid at 80°–90° *α-naphthylamine*-2 : 4 : 6-*trisulphonic acid* is obtained.

(xi.) *α*-**Naphthylamine**-4 : 7-**disulphonic acid** (*Dahl's* No. III. *acid*) is obtained, mixed with about 30 p.c. of the No. II. acid (*v.* 4 : 6-disulphonic acid), by adding sieved *α*-naphthylamine-4-sulphonic acid slowly to 3·5 times its weight of 25 p.c. anhydro-acid below 30° and stirring for 2–3 days or until 6 drops of the melt added to 10 c.c of water give a solution which remains clear at the end of 6 hours. The product converted into dry calcium salt and powdered is extracted with 10 times its weight of 85 p.c. alcohol to remove No. II. salt, the residue being No. III. salt (Dahl, D. R.-P. 41957).

It is also formed when *α*-naphthylamine-7-sulphonic acid is sulphonated with monohydrate at 100°–150° (Cassella, D. P. Anm. C. 3939), or 25 p.c. anhydro-acid at 50°–60° (Bayer, D. P. Anm. F. 6550; Eng. P. 15223 of 1893); *or* when 1 : 8-dinitronaphthalene is digested with 40 p.c. sodium bisulphite solution and 25 p.c. ammonia solution at 80°–90° for 8 hours, the filtrate stirred with about one-third of its weight of concentrated hydrochloric acid for half a day to decompose the sulphamino-acids which result, and the separation recrystallised from water in which the 4 : 7-disulphonic acid is only sparingly, but the 2 : 4 : 7-trisulphonic acid so easily soluble as to need salting out from the solution (Höchst, D. R.-P. 215338); *or* when the bisulphite method is applied to sodium *α*-naphthol-4 : 7-disulphonate (Badische, D. R.-P. 117471; Eng. P 1387 of 1900; *v.* p. 416).

Identification.—The *barium* salt BaA, in needles, and *calcium* salt $CaA+H_2O$ are sparingly soluble in water; the *potassium* salt K_2A+3H_2O, in efflorescent prisms, and *sodium* salt Na_2A+3H_2O, in efflorescent needles, are readily soluble in water, the *acid sodium* salt, in needles, is soluble in 140 parts of water at 20°, or 20 parts at the boiling-point, but like the calcium salt, is insoluble in 85 p.c. alcohol (Dahl, *l.c.*; Erdmann, Annalen, 1893, 275, 220). The solutions of the acid and salts show blue fluorescence. It is convertible into *α-chloronaphthalene*-4 : 7-*disulphonyl chloride*, rectangular prisms, m.p. 107°, and 1 : 4 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 17).

Reactions.—It couples with diazotised bases. From its *diazo-* compound or by the bisulphite method, *α-naphthol*-4 : 7-*disulphonic acid* can be obtained. Heated with aniline (or *p*-toluidine) at 180°, it forms *phenyl-* (or *p-tolyl-*) *α-naphthylamine*-7-*sulphonic acid* by elimination of the 4-sulphonic group. By sulphonation with 35 p.c. anhydro-acid at 80°–90° it yields *α-naphthylamine*-2 : 4 : 7-*trisulphonic acid.*

(xii.) *α*-**Naphthylamine**-4 : 8-**disulphonic acid** ([δ-]*acid*; *disulpho-acid*-S) is formed from *α*-naphthylamine-8-sulphonic acid by sulphonation with 3 times its weight of 10 p.c. anhydro-acid at first in the cold and afterwards at 100° (Schöllkopf, D. R.-P. 40571; Eng. P. 15775 of 1885); also, mixed with the 6 : 8-disulphonic acid, when acetyl-*α*-naphthylamine-8-sulphonic acid is sulphonated with 25 p.c. anhydro-acid in the cold, the product de-acetylated by boiling it with water, and the sodium salt separated from the more soluble 6 : 8-isomeride by fractional crystallisation (Bayer, D. R.-P. 75084). From *α*-naphthol-4 : 8-disulphonic acid, it can be obtained by the bisulphite method (Badische, D. R.-P. 117471; Eng P. 1387 of 1900; *v.* p. 416).

Preparation.—It is obtained by reduction of *α* nitronaphthalene-4 : 8-disulphonic acid, and is present therefore, with the 3 : 8-disulphonic acid (*q.v.*), in the product formed when the sulphonation melt containing naphthalene-1 : 5- and 1 : 6-disulphonic acids is nitrated, and the nitro-acids are reduced. If the sulphonation melt contained naphthalene-*α*-sulphonic acid owing to incomplete disulphonation, sodium *α*-naphthylamine-8-sulphonate will be present in the crude 4 : 8-disulphonate, but can be removed by fractional crystallisation owing to its sparing solubility in water, the more soluble disulphonate being precipitated from the concentrated mother liquor as acid sodium salt on acidification (Aktienges., D. R.-P. 45776; Eng. P. 4625 of 1888; Bernthsen, Ber. 1889, 22, 3327; Paul, Z. angew. Chem. 1896, 9, 563).

Identification.—The *normal sodium* salt Na_2A+2H_2O, forms needles readily soluble in water (Bernthsen, Ber. 1890, 23, 3090, footnote); the *acid sodium* salt scales sparingly soluble in cold water. It is convertible into *α-chloronaphthalene*-4 : 8-*disulphonyl chloride*, flat prisms, m.p. 137°, and 1 : 4 : 5-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 126).

Reactions.—It couples easily with diazotised bases. From the *diazo-* compound, or by the bisulphite method, *α-naphthol*-4 : 8-*disulphonic acid* can be obtained. Fusion with caustic soda at 200° converts it into 1-*amino*-8-*naphthol*-4-*sulphonic acid*, but digestion with 60 p.c. caustic soda solution at 250° furnishes 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid.*

When heated with aniline (or *p*-toluidine) at 180° it yields *phenyl-* (or p-*tolyl-*) *α-naphthylamine*-8-*sulphonic acid* by elimination of the 4-sulphonic group, but this group is retained and the 8-sulphonic group removed, *α-naphthylamine*-4-*sulphonic acid* being the product, when desulphonation is effected by sodium amalgam in the cold, or by zinc-dust and dilute caustic soda solution at the boiling-point. By sulphonation with 40 p.c. anhydro-acid, it forms *naphthasultam*-2 : 4-*disulphonic acid.*

(xiii.) *α*-**Naphthylamine**-5 : 7-**disulphonic acid** is obtained when *α*-naphthylamine-5-sulphonic acid (1 pt.), after acetylation, is mixed with 30 p.c. anhydro acid (8 pts.), or acetyl-*α*-naphthylamine (1 pt.) with 35 p.c. anhydro-acid (5 pts.), at 0°–5°; the mixture kept at 20°–30° for 15–20 hours until a sample, boiled with water, shows no separation of monosulphonic acid in the cold; and the product, after de-acetylation by boiling the melt with water (10 pts.), converted into acid sodium salt by saturating the hot solution with common salt. The *acid sodium* salt $NaH_3A_2+5H_2O$, needles, is very soluble but the *acid barium* salt almost insoluble in cold water.

Reactions.—In alkaline solution it couples readily with diazotised bases. From its *diazo*-compound or by the bisulphite method, *α-naphthol*-5 : 7-*disulphonic acid* can be obtained. Digestion with 75 p.c. caustic soda solution at 170°–180° converts it into 1-*amino*-5-*naphthol*-7-*sulphonic acid.* By sulphonation with 40 p.c. anhydro-acid at 120°–130°, it gives *α-naphthylamine*-2 : 5 : 7-*trisulphonic acid.*

(xiv.) α-**Naphthylamine**-5 : 8-**disulphonic acid** is obtained from α-nitronaphthalene-5 : 8-disulphonic acid by reduction in acid solution. The product, converted into sodium salt, gives in concentrated solution a precipitate of the acid sodium salt on acidification. Both the *acid* and the *acid sodium* salt $NaHA+1\frac{1}{2}H_2O$ form needles very sparingly soluble in water, but easily soluble in alkalis, giving greenish-yellow solutions (Bayer, D. R.-P. 70857 ; Gattermann, Ber. 1899, 32, 1156).

Reactions.—It couples easily with diazotised bases. From its *diazo*- compound *naphthalene*-1 : 4 : 8-*trisulphonic acid* and *naphthasultone*-5-*sulphonic acid* can be obtained, and by the bisulphite method it yields the corresponding *α-naphthol*-5 : 8-*disulphonic acid.* Digestion with 75 p.c. caustic potash solution at 150°–160° converts it into 1-*amino*-8-*naphthol*-5 *sulphonic acid*, but with 60 p c. solution at 250° into 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid.* With sodium amalgam *α-naphthylamine* is obtained (Gattermann, *l.c.*). By sulphonation with 40 p.c. anhydro-acid at 80°–90° it forms *naphthasultamdisulphonic acid*-D.

(xv.) α-**Naphthylamine**-6 : 8-**disulphonic acid** can be obtained from α-naphthylamine-4 : 6 : 8-trisulphonic acid by boiling it with 75 p.c. sulphuric acid (Kalle, D. R.-P. 83146) ; and is formed together with the 4 : 8-disulphonic acid when acetyl-α-naphthylamine-8-sulphonic acid is sulphonated with 25 p.c. anhydro-acid at the ordinary temperature, and the product boiled with water. The sodium salt is much more soluble than that of the 4 : 8-disulphonic acid and, after removal of the latter by crystallisation from the concentrated solution, is separated as acid sodium salt from the filtrate by acidification. The salts in solution show green fluorescence ; the *acid sodium* salt NaHA, in needles, is easily soluble (Bayer, D. R.-P. 75084).

Reactions.—It couples easily with diazotised bases. From its very soluble *diazo*- compound, *naphthasultone*-6-*sulphonic acid*, and by elimination of the amino- group, *naphthalene*-1 : 3-*disulphonic acid* can be obtained. Digestion with 50 p.c. caustic potash solution at 180°–200° converts it into 1-*amino*-8-*naphthol*-6-*sulphonic acid.*

α-Naphthylaminetrisulphonic Acids.

(i.) α-**Naphthylamine**-2 : 4 : 6-**trisulphonic acid** is formed when α-naphthylamine-6-sulphonic acid, or 4 : 6-disulphonic acid, is heated with 25 p.c. anhydro-acid (3·5 pts.) at 50°–60°, and afterwards with 70 p.c. anhydro-acid (1 pt.) at 80°–90°. The *acid sodium* salt forms needles ; it shows blue fluorescence in solution (Bayer, D. P. Anm. F. 7016 ; Eng. P. 15223 of 1893).

Reactions.—It does not couple with diazotised bases (Bayer, *l.c.*). Heated with mineral acids it is converted into *α-naphthylamine*-2 : 6-*disulphonic acid* (Bayer, D. P. Anm. F. 31910), but with sodium amalgam in the cold it gives *α-naphthylamine*-2 : 4-*disulphonic acid.*

(ii.) α-**Naphthylamine**-2 : 4 : 7-**trisulphonic acid.** To obtain this acid, α-naphthylamine-4-sulphonic acid is heated with 40 p.c. anhydro-acid at 120° (Hochst, D. R.-P. 22545 ; Eng. P. 2178 of 1882 ; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 125), *or* α-naphthylamine-7-sulphonic acid (or 4 : 7-disulphonic acid) is heated with 25 p.c. anhydro-acid (3·5 pts.) at 50°–60°, and afterwards with 70 p.c. anhydro-acid (1 pt.) at 80°–90° (Bayer, D. P. Anm. F. 6550 ; Eng. P. 15223 of 1893). It is also formed when 1 : 8-dinitronaphthalene is heated with sodium bisulphite solution and ammonia at 80°–90°, and after removal of the less soluble sodium α-naphthylamine-4 : 7-disulphonate (*q.v.*) by crystallisation, the 2 : 4 : 7-trisulphonate is separated from the mother liquor by salting out (Höchst, D. R.-P. 215338). The *acid sodium* salt forms small needles, shows blue fluorescence in alkaline solution, and does not couple with diazotised bases.

Reactions.—From its *diazo*- compound, *α-naphthol*-2 : 4 : 7-*trisulphonic acid*, and by elimination of the amino- group, *naphthalene*-1 : 3 : 6-*trisulphonic acid* are obtained. By digestion with water at 230° it yields *α-naphthylamine*-2 : 7-*disulphonic acid*, but when boiled with 75 p.c. sulphuric acid, the 7-*monosulphonic acid*

(iii.) α-**Naphthylamine**-2 : 5 : 7-**trisulphonic acid** is obtained when α-naphthylamine-5-sulphonic acid is sulphonated with 35 p.c. anhydro-acid at 90°–120° (Cassella, D. R.-P. 188505), *or* when α-naphthylamine-2 : 5- or 5 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 120°–130° (Bayer, D. P. Anm. F. 7001 ; Eng. P. 17141B of 1893). Its *acid disodium* salt, isolated from the diluted sulphonation product by salting out, forms needles easily soluble in water, and, like the acid, shows green fluorescence in solution.

Reactions.—Digestion with 50 p.c. caustic potash solution at 180°–200° converts it into 1-*amino*-5-*naphthol*-2 : 7-*disulphonic acid.* When desulphonated either by sodium amalgam in the cold or by boiling with zinc-dust and dilute caustic soda solution it yields *α-naphthylamine*-2 : 7-*disulphonic acid.*

(iv.) α-**Naphthylamine**-3 : 5 : 7-**trisulphonic acid** is prepared by reduction of α-nitronaphthalene-3 : 5 : 7-trisulphonic acid (Cassella, D. R.-P. 75432). Its salts are easily soluble and in solution show green fluorescence.

Reactions.—From its *diazo*- compound *naphthalene*-1 : 3 : 7-*trisulphonic acid* and *α-naphthol*-3 : 5 : 7-*trisulphonic acid* can be obtained. Fusion with caustic soda at 160°–170° converts it into 1-*amino*-5-*naphthol*-3 : 7-*disulphonic acid.* When desulphonated either by sodium amalgam in the cold or by boiling with zinc-dust and dilute caustic soda solution it gives *α-naphthylamine*-3 : 7-*disulphonic acid.*

(v.) α-**Naphthylamine**-3 : 6 : 8-**trisulphonic acid**, obtained by reduction of α-nitronaphthalene-3 : 6 : 8-trisulphonic acid (Koch, D. R.-P. 56058; Eng. P. 9258 of 1890), is also formed when sodium α-nitronaphthalene-3 : 8-disulphonate is warmed with sodium bisulphite solution (Fischesser, D. R.-P. 76438; Eng. P. 7046 of 1894).

Preparation.—The product obtained by nitrating the trisulphonation melt consisting largely of naphthalene-1 : 3 : 6-trisulphonic acid, after dilution with water, is neutralised by lime, converted into sodium salt and the filtrate after acidification reduced hot by iron borings. After removal of the iron, the filtrate is concentrated, saturated with salt and acidified, whereby a complete separation of the 3 : 6 : 8-trisulphonic acid as acid sodium salt is achieved, the mother liquor containing nothing of any technical value (Heumann, Anilinfarben, 1898, ii, 539).

Identification.—The *acid disodium* salt Na_2HA forms needles, moderately soluble in water but almost insoluble in hydrochloric acid or brine, and the *sodium* salt Na_3A+3H_2O easily soluble scales (Dressel and Kothe, Ber. 1894, 27, 2147).

Reactions.—From its *diazo-* compound, *naphthalene*-1 : 3 : 6-*trisulphonic acid* (Dressel and Kothe, *l.c.*) and *naphthasultone*-3 : 6-*disulphonic acid* can be obtained. Digestion with water at 180°–250° converts it into *α naphthol*-3 : 6 : 8-*trisulphonic acid*, and with 30–40 p.c. caustic soda solution at 210° into 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid.*

Digestion with ammonia at 160°–180° furnishes 1 : 3-*diaminonaphthalene*-6 : 8-*disulphonic acid*, and with aniline (or *p*-toluidine) at 150°–160° *diphenyl*- (*di*-p-*tolyl*-)1 : 3-*diaminonaphthalene*-6 : 8-*disulphonic acid.* By sulphonation with 25 p.c. anhydro-acid at 70°–80° it yields *naphthasultam*-3 : (4) · 6-*trisulphonic acid.* When desulphonated by boiling it with zinc-dust and dilute caustic soda solution, *α-naphthylamine*-3 : 6-*disulphonic acid* is the product.

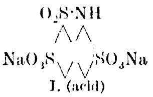
(vi.) α-**Naphthylamine**-4 : 6 : 8-**trisulphonic acid** is obtained by reduction of α-nitronaphthalene-4 : 6 : 8-trisulphonic acid (Bayer, D. P. Anm. F. 7006; D. R.-P. 80741; Eng. P. 17141c of 1893; Kalle, D. R.-P 82563; 99164; Eng. P. 515 of 1894).

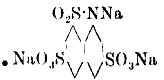
Preparation.—The nitration product obtained from the naphthalene-1 : 3 : 5-trisulphonic acid melt, after dilution with water, is neutralised by lime, and the filtrate, after acidification, reduced hot by iron borings, rendered alkaline by lime, and converted into sodium salt. From the concentrated solution of this salt, the acid sodium salt separates on the addition of hydrochloric acid.

Reactions.—It does not couple with diazotised bases. From its *diazo-* compound, *naphthalene*-1 : 3 : 5-*trisulphonic acid* (Kalle, *l.c.*) and *naphthasultone*-4 : 6-*disulphonic acid*, which is also formed by the bisulphite method, have been obtained. Boiled with 75 p.c. sulphuric acid it gives *α-naphthylamine*-6 : 8-*disulphonic acid*, and digested with water at 160°–220° *α-naphthol*-6 : 8-*disulphonic acid*, the 4-sulphonic group being eliminated in both reactions, but when desulphonated by boiling with zinc-dust and dilute caustic soda solution it is converted into *α-naphthylamine*-4 : 6-*disulphonic acid.* Digested with 70 p.c. caustic soda solution at 175° it furnishes 1-*amino*-8-*naphthol*-4 : 6-*disulphonic acid.* By sulphonation with 25 p.c. anhydro-acid, it gives *naphthasultam*-(2) : 4 : 6-*trisulphonic acid.*

NAPHTHASULTAM DERIVATIVES.

Introductory.—When warmed with anhydro-acid, α-naphthylaminesulphonic acids in which one of the sulphonic groups occupies the *peri*-position relatively to the NH_2 radicle may undergo dehydration, forming naphthasultams, in addition to further sulphonation. Contrasted with the sultones (p. 470), the stability of the sultams is remarkable. Neither by boiling a sultam with caustic alkali solutions, nor by heating it with ammonia is the anhydride ring attacked, although disruption of this ring (accompanied usually by partial desulphonation) can be effected if mineral acids be employed. These naphthasultamsulphonic acids, although not diazotisable, can be coupled with diazotised bases, provided the 4- position be free. The salts are of two types:


I. (acid)


II. (normal)

Those of type I. are colourless, but those of type II. are yellow and give yellow solutions, which show intense green or yellowish-green fluorescence.

(i.) **Naphthasultam** has been obtained from α-naphthylamine-8-sulphonic acid by dehydration with phosphorus oxychloride. It melts at 177°–178°, and in its behaviour towards chlorine presents many analogies to α-naphthol. On nitration, it yields 2 : 4-*dinitronaphthasultam*, pale yellow prisms soluble in caustic alkalis or alkali carbonates but almost insoluble in water (Dannerth, J. Amer. Chem. Soc. 1907, 29, 1320; Bayer, D. R.-P. 210222; *cf.* Zincke and Jülicher, Annalen, 1916, 411, 195; Zincke and Schürmann, *ibid.* 1918, 416, 75).

(ii.) **Naphthasultam**-2 : 4-**disulphonic acid**-S is obtained when α-naphthylamine-8-sulphonic or 4 : 8-disulphonic acid is sulphonated with 25-40 p.c. anhydro-acid at 80°–90°, the operation being continued until a sample of the product diluted with water neither reacts with nitrite nor couples with diazotised bases (Bayer, D. R.-P. 79566; Eng. P. 4979 of 1893; Aktienges., D. P. Anm. A. 3346; Eng. P. 2984 of 1893; Dressel and Kothe, Ber. 1894, 27, 2139). The corresponding α-naphthylamine-2 : 4 : 8 trisulphonic acid is unknown.

Identification.—The *acid disodium* salt Na_2HA+2H_2O forms colourless needles, soluble in water without fluorescence, and the *trisodium* salt $Na_3A+8\frac{1}{2}H_2O$, yellow scales, easily soluble in water with green fluorescence.

Reactions.—Fusion with caustic soda at 170°–180° converts it into 1-*amino*-8-*naphthol*-2 : 4-*disulphonic acid.* Digestion with 40 p.c. sulphuric acid at 110° furnishes *α-naphthylamine*-2 : 8-*disulphonic acid*, but with 20 p.c. hydrochloric acid at 140°–150° *α-naphthylamine*-8-*sulphonic acid.* When heated in 50 p.c. sulphuric acid solution at 75°–80° with nitric acid of sp.gr. 1·2, it is converted successively into *nitronaphthasultamsulphonic acid* and 2 : 4-*dinitronaphthasultam* (Bayer, D. R.-P. 210222).

(iii.) **Naphthasultam**-3 : 6-**disulphonic acid** is prepared by boiling the acid sodium salt of naphthasultam-3 : (4) : 6-trisulphonic acid with 20 p.c. sulphuric acid. The *trisodium* salt Na_3A+4H_2O forms easily soluble, small, yellow prisms (Bayer, D. R.-P. 84139; Dressel and Kothe, Ber. 1894, 27, 2149).

Reactions.—Fusion with caustic soda at 180° converts it into 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid.* When boiled with 50 p.c. sulphuric acid, it gives α-*naphthylamine*-3 : 6 : 8-*trisulphonic acid.*

(iv.) **Naphthasultamdisulphonic acid**-ε, obtained by heating sodium α-naphthylamine-3 : 8-disulphonate with 40 p.c. anhydro-acid at 80°-90°, has not been described (Bayer, D. R.-P. 79566; Eng P. 4979 of 1893).

(v.) **Naphthasultamdisulphonic acid**-D, obtained by heating sodium α-naphthylamine-5 : 8-disulphonate with 40 p c. anhydro-acid at 80°-90°, yields 1-*amino*-8-*naphtholdisulphonic acid*-D on fusion with caustic soda at 170° (Bayer, D. R.-P. 79566; 80668; Eng. P. *l.c.*)

(vi.) **Naphthasultam** - 3 : (4) : 6 - **trisulphonic acid** is formed when the acid sodium salt of α-naphthylamine-3 : 6 : 8-trisulphonic acid is heated with 25 p c. anhydro-acid at 80° until a test no longer reacts with nitrite. The *acid sodium* salt Na_3HA+4H_2O and the yellow *sodium* salt Na_4A+4H_2O are easily, but the yellow *barium* salt is only very sparingly soluble (Bayer, D. R.-P. 84139; Dressel and Kothe, Ber. 1894, 27, 2147).

Reactions.—Digestion with 75 p c. caustic potash solution at 130° converts it into 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid.* When boiled with 20 p.c. sulphuric acid it yields *naphthasultam*-3 : 6-*disulphonic acid*; and with 50 p.c. sulphuric acid α-*naphthylamine*-3 : 6 . 8 *trisulphonic acid* (Bayer, *l c.*; Dressel and Kothe, *l.c.*).

(vii.) **Naphthasultam** - (2) : 4 : 6 - **trisulphonic acid** is obtained when the acid sodium salt of α-naphthylamine-4 : 6 : 8-trisulphonic acid is heated with 25 p.c. anhydro-acid at 80°–90° until a test no longer reacts with nitrite (Bayer, D. R.-P. 84140). The *acid sodium* salt forms easily soluble needles; the *sodium* salt Na_4A+6H_2O, easily soluble, minute yellow prisms. When heated with caustic alkali at 150°–160°, it is converted into 1-*amino*-8-*naphthol*-(2) : 4 : 6-*trisulphonic acid* (Bayer, D. R.-P. 84597).

CHLORO-α-NAPHTHYLAMINES.

8-**Chloro**-α-**naphthylamine** can be obtained from 1 : 8-diaminonaphthalene by allowing its azimino-derivative to interact with copper powder or with cuprous salts and hydrochloric acid at 30°. The base forms needles, m.p. 98° (Badische, D. R.-P. 147852; *cf.* Atterberg, Ber. 1876, 9, 1730).

5:8-**Dichloro**-α-**naphthylamine,** formed by reduction of 5:8-dichloro-α-nitronaphthalene, gives needles, m.p. 104° (Widman, Bull. Soc. chim. 1877, [ii.] 28, 510; Bayer, D. R.-P. 293318).

8-**Chloro** - α - **naphthylamine** - 5 - **sulphonic acid** is formed from the azimino-derivative of 1 : 8-diaminonaphthalene-4-sulphonic acid by interaction with copper powder (Badische, *l.c.*). When digested with 50 p.c. caustic soda solution at 190°–195° it yields 1-*amino*-8-*naphthol*-5-*sulphonic acid* (Badische, D. R.-P. 112778).

Several α-chloro-α-naphthylaminesulphonic acids, prepared by nitrating α-chloronaphthalenesulphonic acids and reducing the products, have been used in making *azo*-dyes, but not described in detail (Read, Holliday & Sons, Eng. P. 13999 of 1897; 11736 of 1898).

8-**Chloro**-α-**naphthylamine**-3 : 6-**disulphonic acid** is prepared from the azimino-derivative of 1 . 8-diaminonaphthalene-3 : 6-disulphonic acid by interaction with copper powder (Badische, D. R.-P. 147852), or from α-naphthylamine-3 : 6-disulphonic acid by conversion into the chloro-acid with subsequent nitration and reduction (Bayer, D. R.-P. 289107) It crystallises from acid solution in needles.

Reactions.—It couples with diazotised bases. Fusion with caustic alkali converts it into 1-*amino*-8-*naphthol*-3 : 6-*disulphonic acid*, but when heated with dilute sulphuric acid under pressure it yields 8-*chloro*-α-*naphthol*-3 : 6-*disulphonic acid.*

Acylated by interaction with *m*-nitrobenzoyl chloride, followed by reduction and condensation with phosgene, it furnishes *carbamide* derivatives (Bayer, *l.c.*).

2 · 4-**Dichloro**-α-**naphthylaminesulphonic acid** is formed when acetyl-2 : 4-dichloro-α-naphthylamine is sulphonated with 23 p.c. anhydro-acid below 45°, and the product de-acetylated by boiling it with water. It is sparingly soluble in water; its *sodium* salt forms scales, and its *zinc* and *magnesium* salts long needles. When its sparingly soluble, crystalline *diazo*-compound is heated with sodium carbonate solution at 60°, it is converted into the *diazo-oxide* of 4-chloro-1-amino-β-naphtholsulphonic acid (Badische, D. R.-P. 153298; Eng. P. 16995 of 1903).

NITRO-α-NAPHTHYLAMINES.

(i.) 2-**Nitro**-α-**naphthylamine** is obtained as acetyl derivative, mixed with acetyl-4-nitro-α-naphthylamine, by nitrating acetyl-α-naphthylamine in acetic acid solution. By limited hydrolysis of the product with aqueous alcoholic caustic potash, 4-nitro-α-naphthylamine can be separated from the acetyl-2-nitro-α-naphthylamine, which is most conveniently hydrolysed by boiling with alcoholic hydrochloric acid (Lellmann and Remy, Ber. 1886, 19, 797; Lellmann, Ber. 1887, 20, 892).

Identification.—It crystallises from alcohol in reddish yellow, monoclinic prisms, m.p. 144°, and its *acetyl* derivative in yellow needles, m.p. 199° (Lellmann, Ber. 1884, 17, 112). When boiled with excess of caustic potash solution it is converted into 2-*nitro*-α-*naphthol.*

(ii.) 4-**Nitro**-α-**naphthylamine,** prepared from acetyl-4-nitro-α-naphthylamine (*v. supra*) by hydrolysis with alcoholic potash (Liebermann, Annalen, 1876, 183, 232), can also be obtained by mixing α-naphthyloxamic acid with nitric acid (sp.gr. 1·36) at 30°–40°, and hydrolysing the product with alkalis or mineral acids (Lange, D. R.-P. 58227); *or* by heating α-chloro-4-nitronaphthalene with 8 p.c. alcoholic ammonia at 150°-170° (Griesheim, D. R.-P. 117006; Eng. P. 7692 of 1900).

Identification.—It crystallises from alcohol in orange needles, m.p. 191°, and its *acetyl* derivative in yellow needles, m.p. 190°. When boiled with aqueous caustic potash, it is converted into 4-*nitro-α-naphthol*.

4-Nitro-α-naphthylamine-5-sulphonic acid, obtained when α-naphthylamine-5-sulphonic acid, dissolved in 20 times its weight of sulphuric acid, is nitrated below 10°, forms sparingly soluble, small needles, and its *sodium* salt yellow scales (Bayer, D. R.-P. 133951; Eng P. 9498 of 1899; *cf.* Levinstein, Eng. P. 13178 of 1899).

4-Nitro-α-naphthylamine-6-sulphonic and 7-sulphonic acids are obtained by the nitration of the corresponding α-naphthylamine-sulphonic acids or their acetyl derivatives in sulphuric acid solution. The 6-sulphonic acid and its salts respectively are less soluble than the 7-isomerides (Cassella, D. R-P. 73502; 74177; Eng P. 15444 of 1893). Diazotised, these acids, singly or mixed, have been used as first component in certain *azo*-dyes.

(iii.) 5-**Nitro**-α-**naphthylamine** can be prepared by partial reduction of 1 : 5-dinitronaphthalene with alcoholic hydrogen sulphide (Beilstein and Kuhlberg, Annalen, 1873, 169, 87), *or* by hydrolysis of 5-nitro-α-naphthylamine-4-sulphonic acid (Nietzki and Zubelen, Ber. 1889, 22, 452), *or*, mixed with the 4- and 8-compounds, by nitration of α-naphthylamine dissolved in 10 times its weight of sulphuric acid (Meldola and Streatfeild, Chem. Soc. Trans. 1893, 63, 1055).

Identification.—It crystallises in small, red needles, m p. 119°, and its *acetyl* derivative in large, brown prisms, m p. 220° (Badische, D. R-P 145191). Its *sulphate* is less soluble than that of the 4- or 8- isomeride

5-Nitro-α-naphthylamine-2-sulphonic acid can be prepared by nitrating α-naphthylamine-2-sulphonic acid in sulphuric acid solution below 15°. The *acid* and its *diazo*- compound are sparingly soluble (Cassella, D. R.-P. 70890).

5-Nitro-α-naphthylamine-4-sulphonic acid is formed when acetyl-α-naphthylamine-4-sulphonic acid, mixed with sulphuric acid, is nitrated in the cold, and the product de-acetylated by boiling it with dilute acid. The *acid* HA crystallises in needles.

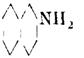
A nitro-α-naphthylaminesulphonic acid, probably isomeric with these acids, is obtained by reduction of 1 : 5-dinitronaphthalene-3-sulphonic acid with sodium sulphite or bisulphite (Hochst, D. R.-P. 117268)

(iv.) 8-**Nitro**-α-**naphthylamine** occurs to the extent of 6–8 p.c. in the product obtained by the nitration of α-naphthylamine in sulphuric acid solution. It crystallises in red scales, m.p. 96°–97°, and its *acetyl* derivative in needles, m.p. 187°–188° (Meldola and Streatfeild, *l.c.*).

(v.) 2 : 4-**Dinitro**-α-**naphthylamine** can be obtained from acetyldinitro-α-naphthylamine by hydrolysis with 50 p.c. sulphuric acid at 100° (Liebermann, Annalen, 1876, 183, 274; Meldola and Forster, Chem. Soc. Proc. 1893, 9, 8); *or* from 2 : 4-dinitro-α-naphthol by heating it with alcoholic ammonia under pressure at 190°–200° (Witt, Ber. 1886, 19, 2033; Morgan and Evens, Chem. Soc. Trans. 1919, 115, 1129). It crystallises in yellow needles, m.p. 237°, and its *acetyl* derivative in yellow needles, m.p. 250°.

Reactions.—When heated with aqueous alkalis, it is converted into 2 : 4-*dinitro-α-naphthol*. Diazotisation in concentrated sulphuric acid solution converts the base or its acetyl derivative into 4-*nitronaphthalene*-1-*diazo*-2-*oxide* (Friedlander, Ber. 1895, 28, 1951; Morgan and Evens, *l.c.*).

(vi.) 4 : 5-**Dinitro**-α-**naphthylamine** is formed by the nitration of acetyl-5-nitro-α-naphthylamine suspended in sulphuric acid, and hydrolysis of the product by boiling with dilute acid. It crystallises in orange scales, m.p. 236°, and its *acetyl* derivative in yellow needles, m.p. 244° (Badische, D. R.-P. 145191; 158499).



(ii.) β-**Naphthylamine** (β-*aminonaphthalene*) was first prepared by reduction of 1-bromo-β nitronaphthalene by tin and hydrochloric acid (Liebermann and Scheiding, Annalen, 1876, 183, 264). It is obtained, mixed with varying proportions of ββ′-dinaphthylamine, when β-naphthol is heated with ammonia at 160° under pressure for 60–70 hours (Badische, D. R.-P. 14612), *or* with twice its weight of ammonia-zinc chloride at 200°–210° for 2 hours (Merz and Weith, Ber. 1880, 13, 1300), *or* with 4 times its weight of anhydrous or hydrated ammonia-calcium chloride at 270°–280° for 8 hours (Benz, Ber 1883, 16, 19), *or*, as dry sodium compound, with ammonium chloride at 200° for 24 hours (Oehler, Eng. P (prov. spec) 2516 of 1880), *or* by the bisulphite method, which requires a pressure of not more than 5–6 instead of 50–60 atmospheres and gives a better yield than the older processes.

Preparation.—β-Naphthol (144 pts.) is heated with 22 p c ammonium sulphite solution (600 pts) and 20 p.c. ammonia (125 pts.) at 100°–150° in an autoclave provided with a stirrer, until in the course of about 8 hours the conversion is complete. Above 150°, ββ′-dinaphthylamine begins to be formed. When cold, the β-naphthylamine is removed by filtration, the filtrate being used for a subsequent operation. It is then extracted by hot dilute caustic soda solution to remove β-naphthol, dissolved in dilute hydrochloric acid in which ββ′-dinaphthylamine is insoluble, recovered from solution by the addition of alkali and finally distilled in a vacuum. The yield is almost quantitative (Badische, D. R.-P. 117471, Eng. P. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 69, 88).

Identification.—It crystallises from alcohol in colourless, lustrous scales, melts at 112°, boils at 294° (Liebermann and Jacobson, Annalen, 1882, 211, 41), is moderately volatile with steam, and dissolves easily in hot but only sparingly in cold water. The solutions of the base show blue fluorescence; those of its salts are non-fluorescent. The *hydrochloride* B·HCl forms non-fluorescent scales, easily soluble, and the *nitrate* $B \cdot HNO_3$ and *sulphate* $B_2 \cdot H_2SO_4$ scales, sparingly soluble in water. The *platinichloride* crystallises in scales, and the *picrate*, from alcohol, in long yellow needles, m.p. 195°. Unlike α-naphthylamine it gives no colour reactions with ferric chloride, chromic acid, bleaching powder, or nitrous acid.

Reactions.—It couples with diazotised bases as the end component of *azo*-dyes. From its *diazo*- compound, *β-naphthol* can be obtained (Liebermann, Annalen, 1876, 183, 268). Its nitrate, by nitration, gives a mixture of 5-*nitro*- and 8-*nitro-β-naphthylamine.* On sulphonation, it furnishes a series of *mono*-, *di*-, and *tri-sulphonic acids.*

Reduction in boiling amyl alcohol solution with sodium converts it into ac.-*tetrahydro-β-naphthylamine* with about 3–4 p.c. of the *ar.*-derivative. When heated alone, or with calcium or zinc chloride, it is converted partially into *ββ′-dinaphthylamine* and ammonia, but with sodamide, mixed with naphthalene at 230°, it gives 1 : 6-*diaminonaphthalene.*

Tests.—β-Naphthylamine should be free from β-naphthol and ββ′-dinaphthylamine, and therefore should be completely soluble in dilute hydrochloric acid. It should also have the right melting-point.

Acyl Derivative.

Acetyl-β-naphthylamine (*acet-β-naphthalide*), obtained together with about 14 p.c. of ββ′-dinaphthylamine when β-naphthol is heated with ammonium acetate at 270°–280° for 8 hours (Merz and Weith, Ber. 1881, 14, 2343; Calm, Ber. 1882, 15, 610), is best prepared by boiling β-naphthylamine with 1·25–1·5 times its weight of glacial acetic acid for 12 hours, the ββ′-dinaphthylamine (about 10 p.c.) formed being readily separated by crystallisation from alcohol, in which it is only sparingly soluble (Liebermann and Jacobson, Annalen, 1882, 211, 42).

Properties.—It crystallises in lustrous scales, m.p. 132° (Cosiner, Ber. 1881, 14, 59), dissolves readily in alcohol, but only sparingly in water, and is more easily hydrolysed by dilute acids than by alkalis (Calm, *l.c.*).

Reactions.—On chlorination, it yields *acetyl-1-chloro-β-naphthylamine.* Nitration converts it into *acetyl-1-nitro-β-naphthylamine.* By sulphonation with sulphuric acid, it furnishes *acetyl-β-naphthylamine-5-sulphonic acid* at 20°–30°, or *acetyl-β-naphthylamine-7-sulphonic acid* at 150°–160° (Kinzlberger, D. P. Anm. K. 5732),[1] but with chlorosulphonic acid *acetyl-β-naphthylamine-4-sulphonyl chloride*, m.p. 192° (Höchst, D. R.-P. 292357).

Alkyl Derivatives.

Methyl-β-naphthylamine, obtained by heating β-naphthol (100 gr.), methylamine hydrochloride (75 gr.), and 5N caustic soda solution (190 c.c.) under pressure at 200°–220°, is an oil, b.p. 317° under 766 mm. or 207° under 60 mm., which yields a *nitrosamine*, needles, m.p. 88°, and an *acetyl* compound, prisms, m.p. 50°–51° (Morgan and Evans, Chem. Soc. Trans. 1919, 115, 1141; *cf.* Pechmann and Heinze, Ber. 1897, 30, 1785; Pschorr and Karo, Ber. 1906, 39, 3142).

Dimethyl-β-naphthylamine, prepared by heating β-naphthylamine (1 mol.) with methyl iodide (3 mols.), caustic soda (2 5 mols.), and water (5 mols.) at 120° for 5–6 hours, converting the quaternary iodide into chloride or hydroxide and evaporating the aqueous solution of either to dryness (Morgan, Chem. Soc. Trans. 1900, 77, 822; *cf.* Bamberger and Muller, Ber. 1889, 22, 1306), forms scales, m.p. 46°, b.p. 305°. Reduction in amyl alcoholic solution with sodium converts it into ar.-*tetrahydrodimethyl-β-naphthylamine*, mixed with a very small amount of the *ac.*-derivative.

Ethyl-β-naphthylamine, obtained by boiling a solution of β-naphthylamine (10 pts.) in alcohol (30 pts.) with ethyl bromide (8·5 pts.) during 12 hours (Fischer, Ber. 1893, 26, 193), is an oil, b.p. 305° under 716 mm., 191° under 25 mm. (Bamberger and Muller, Ber. 1889, 22, 1297), or 315°–316° under 760 mm. (Vaubel, Chem. Zeit. 1903, 27, 278).

Reactions.—It couples with diazotised bases furnishing *azo*- dyes. Reduction in amyl alcoholic solution with sodium converts it into a mixture of ar.- and ac-*tetrahydroethyl-β-naphthylamine*, the *ar.*-derivative being the chief product. On sulphonation[2] with weak anhydro-acid at a moderate temperature, the 5-*sulphonic acid*, mixed with a small quantity of the 8-*sulphonic acid*, is formed; with monohydrate at 140° the 7-*sulphonic acid* is obtained; and with 20 p.c. anhydro-acid at 110°–120°, the 5 : 7-*disulphonic acid*[3] is produced.

Diethyl-β-naphthylamine, obtained by heating β-naphthylamine (39 gr.), caustic soda (22 gr.), water (22 c.c.), and ethyl iodide (85 gr.) at 120° during 7–8 hours (Morgan, Chem. Soc. Trans. 1900, 77, 823), is an oil, b.p. 316° under 717 mm., which on reduction in amyl alcoholic solution by sodium furnishes ar.- mixed with only a small amount of ac.-*tetrahydrodiethyl-β-naphthylamine* (Bamberger and Williamson, Ber. 1889, 22, 1760).

Aryl Derivatives.

Phenyl-, tolyl-, and other aryl-β-naphthylamines can be prepared by heating β-naphthol with the respective base (or its hydrochloride) under pressure at 200°–210° for 10 hours either alone (Graebe, Ber. 1880, 13, 1850; Badische, D. R.-P. 14612; *cf.* Oehler, Eng. P. 2516 (prov. spec.) of 1880), or with the addition of ammonia-zinc chloride (Merz and Weith, Ber. 1880, 13, 1300). The yield is almost quantitative when β-naphthol (1 mol.), the base (2 mols.), and anhydrous calcium chloride (1 mol.) are heated together at 280° under pressure for 9 hours (Friedlander, Ber. 1883, 16, 2077), *or* when β-naphthol and the base are heated together with 1 p.c. of iodine at 180°–190° during several hours (Knoll & Co., D. R.-P. 241853; Knoevenagel and Sakow, J. pr. Chem. 1914, [ii.] 89, 17). These products dissolve in the ordinary organic solvents, and, when heated with hydrochloric acid under pressure at 240°, regenerate β-naphthol and the base (Friedländer, *l.c.*).

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[1] Acetyl-β-naphthylaminesulphonic acids are also obtained when sodium β-naphthylamine-5-, 6-, 7-, or 8-sulphonate in aqueous solution is warmed with acetic anhydride at 50°–60° for a few minutes. The sodium salts, obtained by salting out, and the acids derived from them by acidification, are crystalline, but much more soluble in water than the corresponding naphthylamine compounds (Hochst, D. R.-P. 129000; Eng. P. 17366 of 1898).

[2] Alkyl-β-naphthylaminesulphonic acids have been obtained by heating solutions of the respective sodium β-naphthylaminesulphonates with the alkyl chloride or sodium alkylsulphate under pressure. The derived *disazo*- dyes are much bluer in shade than those from the non-alkylated acids (Bayer, D. R.-P. 41506).

[3] Ethyl-β-naphthylamine-5 : 7-disulphonic acid is not desulphonated either by sodium amalgam in the cold or by dilute acid at 160°–170°; when fused with caustic alkali it yields *ethyl-2-amino-5-naphthol-7-sulphonic acid* (Leonhardt, D. R.-P. 95624; Eng. P. 10669 of 1895).

Phenyl-β-naphthylamine is obtained when β-naphthol (144 pts.), aniline (170 pts.), and iodine (1–2 pts.) are heated together at 180°–190° during 7 hours, and the product, after successive extractions by dilute acid and by dilute caustic soda solution, is distilled in a vacuum (Knoll & Co., *l.c.*).

Identification.—It forms needles, m.p. 108°. b.p. 395° (Crafts, Annalen, 1880, 202, 5) or 237° under 15 mm. (Knoll & Co., *l.c.*), is moderately soluble in cold solvents, and in solution shows blue fluorescence. The *hydrochloride* is a crystalline powder, decomposed by water. The *acetyl* derivative, m.p. 93° (Streiff, Annalen, 1881, 209, 157) has been used as a stabiliser for nitrocellulose powders (Ryan and Drumm, Proc. Roy. Irish Acad. 1918, 34, [B] (8), 165). The *nitroso-* derivative forms prisms, m.p. 93° (Streiff, *l.c.*). The *toluene-p-sulphonyl* derivative, m.p. 133°, readily furnishes 1-*nitro-* and 1 : 6-*dinitro-β-naphthylamine* (Morgan and Micklethwait, Chem. Soc. Trans 1912, 101, 148; Aktienges., D. R.-P. 164130; Eng. P. 27497 of 1904).

Reactions.—It couples with diazotised bases forming *azo-* dyes. When sulphonated with 4 times its weight of monohydrate below 50°, it yields a mixture of the 5- and 8-*monosulphonic acids* (Zimmer, D. R.-P. 45940; Eng. P. 13798 of 1888; Clayton Aniline Co., D. R.-P. 53649; Eng. P. 10934 of 1889; Lesser, Ber. 1894, 27, 2364; Bayer, D. R.-P. 70349; Eng. P. 7337A of 1892).

o-Tolyl-β-naphthylamine, prepared similarly to the phenyl derivative, forms scales, m.p. 95°, b.p. 235°–237° under 14 mm. (Knoll & Co., D. R.-P. 241853). On sulphonation below 50° it gives a mixture of the 5- and 8-*monosulphonic acids* (Clayton Aniline Co., D. R.-P. 57370; Eng. P. 5155 of 1890; *cf.* Bayer, *l.c.*).

p-Tolyl-β-naphthylamine forms scales, m.p. 103°, showing in solution blue fluorescence; its *acetyl* derivative, needles, m.p. 85° (Friedlander, Ber. 1883, 16, 2079).

Of the *phenyl-*(o- or p-*tolyl-*)*β-naphthylaminesulphonic acids*, the 5-, 6-, 7-, or 8-sulphonic, and the 3 : 6- or 6 : 8-disulphonic acid can be obtained by heating the corresponding β-naphthylaminesulphonic acid with aniline (*o-* or *p*-toluidine) and its hydrochloride at 160°–170° (Bayer, D. R.-P. 70349, 71158, 71168; Eng. P. 7337A of 1892). Less satisfactory results follow when the corresponding β-naphtholsulphonic acid is heated with the base and its hydrochloride at 190°–200° (Aktienges., D. R.-P. 38424), but if the bisulphite method is used good yields are obtained (Badische, D. R.-P. 122570; Eng. P. 18726 of 1900). The acids are moderately soluble in hot water; the sodium salts may be separated from solution by salting out. When coupled with diazotised bases they form *azo-* dyes which are bluer in shade than those from aryl-α-naphthylaminesulphonic acids.

ββ′-Dinaphthylamine[1] is formed (3·5 p.c.) when β-naphthylamine is heated at 280°–300° during 8 hours (Benz, Ber. 1883, 16, 14); and in larger amount when it is heated with calcium chloride at 260°–280° (Merz and Weith, Ber. 1881, 14, 2343), or boiled with glacial acetic acid for some hours (Liebermann and Jacobson, Annalen, 1882, 211, 43), or heated at 170°–190° in a current of hydrogen chloride (Klopsch, Ber. 1885, 18, 1586). A by-product in the manufacture of β-naphthylamine, it is obtained in large amount when β-naphthol is heated with ammonia-zinc chloride at 280° (Merz and Weith, *l.c.*; Calm, Ber. 1882, 15, 614; Benz, *l.c.*), *or* with β-naphthylamine (Badische, D. R.-P. 14612), *or* with β-naphthylamine and calcium chloride at 270°–280° (Benz, *l.c.*).

Preparation.—An almost quantitative yield is obtained by boiling a solution of β-naphthylamine (1 pt.) in alcohol (6 pts.) with sodium bisulphite solution of 40°Bé (6 pts.) in a reflux apparatus for 24 hours (Bayer, D. R.-P. 114974; Eng. P. 22804 of 1899), or by heating β-naphthylamine with 0·5 p.c. of iodine at 230° during 4 hours (Knoll & Co., D. R.-P. 241853; Knoevenagel, J. pr. Chem. 1914, [ii.] 89, 23).

Properties.—It crystallises in scales, m.p. 171°, b.p. 471° (Ris, Ber. 1887, 20, 2619). Dissolved in alcohol or benzene, it shows intense blue fluorescence. When heated with hydrochloric acid at 240°, it yields β-naphthylamine and β-naphthol quantitatively (Ris, Ber. 1886, 19, 2017), and, with sulphuric acid, mixtures of the isomeric β-naphthylamine- and β-naphtholsulphonic acids (Sandoz, D. R. P. 64859).

The 7 : 7′-*disulphonic acid* has been prepared from β-naphthylamine-7-sulphonic acid by the bisulphite method (Bayer, *l.c.*); the 5 : 5′-*dihydroxy*-7 : 7′-*disulphonic acid* from 2-amino-5-naphthol-7-sulphonic acid by the bisulphite method (Bayer, *l.c.*), or by heating it with water under pressure at 200°; and the 8 : 8′-*dihydroxy*-6 : 6′-*disulphonic acid* from 2-amino-8-naphthol-6-sulphonic acid by the latter method (Bayer, D. R.-P. 121094; Eng. P. 24296 of 1899). The dihydroxy- compounds couple with diazotised bases, yielding *azo-* dyes (*cf.* Bayer, D. R.-P. 114841; 221124; Eng. P. 24296 of 1899).

β-Naphthylaminesulphonic Acids

Introductory. — β-Naphthylaminesulphonic acids are obtained by the following methods:—

(1) By sulphonation of β-naphthylamine or of the derived β-naphthylaminesulphonic acids. The product in most cases is a mixture of acids, from which the more soluble constituents cannot easily be obtained pure.

(2) By heating the sodium salts of the corresponding β-naphtholsulphonic acids with ammonia under pressure. Except with β-naphthol-1-sulphonic acid and its derivatives, this reaction gives a satisfactory yield of a pure product, and the ease with which it takes place increases with the number of sulphonic groups in the molecule.

(3) By heating the sodium salts of the corresponding β-naphtholsulphonic acids with ammonium bisulphite solution and ammonia at 100°–150° (*v.* p. 416). The process is applicable to all acids which do not contain a 4-sulphonic group, and is of value for the production of the

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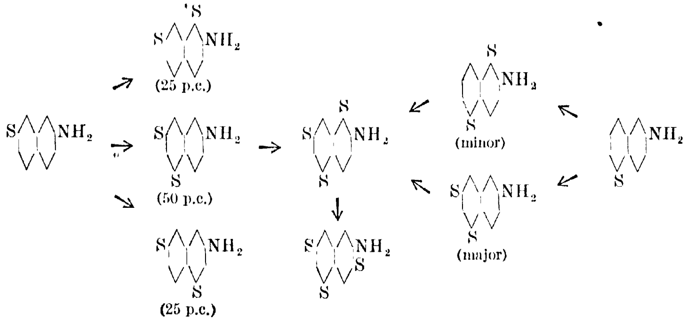
[1] *αα′-Dinaphthylamine*, obtained by heating α-naphthylamine with its hydrochloride at 150°, forms scales, m.p. 113° (Girard and Vogt, Bull. Soc. chim 1872, [ii.] 18, 68; *cf.* Calm, Ber. 1882, 15, 615; Benz, Ber. 1883, 16, 16). *αβ′-Dinaphthylamine*, obtained by heating α-naphthylamine with β-naphthol and calcium chloride, forms prisms, m.p. 110°–111° (Benz, *l.c.*).

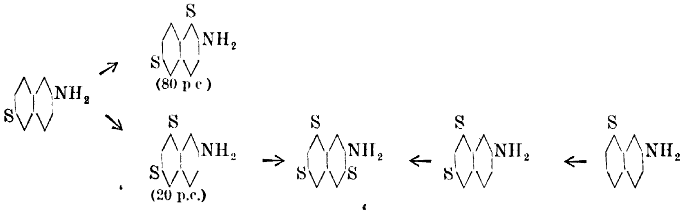
6-, or 7-, or 8-monosulphonic acid, as each of the corresponding β-naphtholsulphonic acids is obtained in a pure state much more easily from β-naphthol than is the β-naphthylaminesulphonic acid from the mixed acids of the sulphonation melt (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 357).

(4) By reduction of β-nitronaphthalenesulphonic acids. Only two acids are obtained in this way, *viz.* the 4 : 7- and the 4 . 8-disulphonic acids, but for the production of the latter no other mode of preparation has been described.

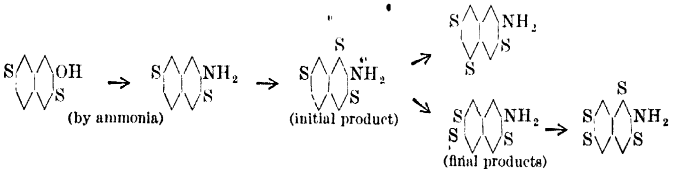
Four monosulphonic acids, all of them heteronucleal, are known to be formed by the sulphonation of β-naphthylamine; six disulphonic acids by the sulphonation of monosulphonic acids; and six trisulphonic acids by the sulphonation of disulphonic acids. For the sulphonation of β-naphthylamine, sulphuric acid is used, but for that of the monosulphonic acids 20 p.c. anhydro-acid, and for that of the disulphonic acids 40 p.c. anhydro-acid are required, the end of the di- or tri-sulphonation being ascertained either by the solubility of the product or by the behaviour of the diazotised acid with R-salt. The effects of concentration of the acid, of temperature and of duration of the reaction on the nature of the product, correspond with those traced out in other cases of sulphonation (*v.* p. 413). It should be noted that sulphonation in the 1-position occurs only when at least one other sulphonic group is present in the molecule, and that the 1-sulphonic group when present is the first to be eliminated by hydrolysis.

The following schemes illustrate the order in which sulphonic groups are introduced into the molecule of the isomeric monosulphonic acids:—





The transformation into the 3 : 5 : 7-trisulphonic acid which β-naphthylamine-1 : 5 : 7-trisulphonic acid undergoes in the presence of 40 p.c. anhydro-acid at 140° is only less remarkable than that which has been shown to occur with the 1 : 3 : 7-trisulphonic acid under similar conditions :—



β-Naphthylaminemonosulphonic acids are very sparingly soluble in water. The di- and tri-sulphonic acids dissolve easily in water, but their acid salts are less soluble, and are precipitated instead of the acids when a mineral acid is added to solutions of their alkali salts.

As sources of azo-dyes, the β-naphthylaminesulphonic acids are less important than the α-compounds. Many of the dyes obtained by coupling them with tetrazo-derivatives are of little value (*cf.* Cassella, D. R.-P. 46711); moreover, the β-sulphonic acids cannot be used as middle components in polyazo- dyes, as the NH_2 radicle, after coupling has taken place in the *ortho*-position relatively to it, does not interact with nitrite to form a diazo- compound, but an azimino-like derivative which is incapable of coupling (*cf.* Bayer, D. R.-P. 79816; Eng. P. 9972 of 1893).

β-Naphthylaminesulphonic acids containing either 1- or 8-sulphonic groups do not form azo-dyes, but diazoamino- compounds when coupled with diazotised bases. Those containing a 1-sulphonic group exchange it for hydroxyl, giving the diazo-oxides of β-amino-α-naphthol derivatives when diazotised and afterwards warmed at 50°–60° with excess (2 mols.) of sodium carbonate solution (*cf.* Badische, D. R.-P. 148882).

β-Naphthylaminesulphonic acids containing a 4-sulphonic group, like the *meta*-sulphonic acids from α-naphthylamine, yield hydroxytoluic acids by prolonged heating with caustic alkali solution at 280°, but, unlike them, are not converted into diaminonaphthalenes when heated under pressure with ammonia.

Unlike α-naphthylaminesulphonic acids which, when digested with caustic alkali solution, exchange the NH_2 for an OH radicle, β-naphthylaminesulphonic acids, under similar conditions, retain the amino- group, exchanging an α-SO_3H for an OH radicle, thus furnishing aminonaphtholsulphonic acids of which they are an important source.

From β-naphthylamine-3 . 6- and 5 : 7-disulphonic acids, carbamide derivatives have been obtained by methods similar to those employed with α-naphthylaminesulphonic acids (Bayer, D. R.-P. 288273; *v.* p. 439).

β-Naphthylaminemonosulphonic Acids.[1]

(i.) β-**Naphthylamine-1-sulphonic acid** (*Tobias's acid*) is obtained when sodium β-naphthol-1-sulphonate is heated with 4–5 times its weight of 15–20 p.c. aqueous ammonia for 20 hours at 220°–230°. The product when cold is filtered to remove β-naphthylamine and the filtrate mixed with hydrochloric acid to precipitate the Tobias acid from unchanged β-naphtholsulphonate (Tobias, D. R.-P. 74688, Eng. P. 15404 of 1893). If, however, the bisulphite method be used, the production of β-naphthylamine is entirely avoided (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357; Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Identification.—The *acid* separates in sparingly soluble anhydrous scales from hot, or in efflorescent hydrated needles from cold water, the *sodium* salt NaA+H_2O in easily soluble scales, which give a non-fluorescent solution (Tobias, *l.c.*). It is convertible into *β-chloronaphthalene 1-sulphonyl chloride*, m.p. 76° (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 238), and 1 : 2-*dichloronaphthalene* (Armstrong and Wynne, *l.c.*; Tobias, *l.c.*).

Reactions.—Diazotised, it forms the first component in certain much used *azo*- dyes (*cf.* Badische, D. R.-P. 112833; Eng. P. 25511 of 1899). From its sparingly soluble, crystalline *diazo*- compound, *β-naphthol*-1-*sulphonic acid* has been obtained (Tobias, *l.c.*). When heated at 230° in a dry neutral atmosphere, its sodium salt is converted into sodium *β-naphthylsulphamate* (Tobias, *l.c.*). On sulphonation with 20 p.c. anhydro-acid it yields *β-naphthylamine*-1 : 5-*disulphonic acid.*

(ii.) β-**Naphthylamine-4-sulphonic acid** is obtained when β-naphthol-4-sulphonic acid is heated with ammonia under pressure (Kalle, D. R.-P. 78603), or, mixed with the 8-sulphonic acid, when β-naphthylamine-4 : 8-disulphonic acid is boiled with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934).

Identification.—The *acid* HA+H_2O crystallises in sparingly soluble, long, white needles; the *potassium* salt KA+1½H_2O in small needles; and the *sodium* salt NaA+4H_2O in scales. The solution of the sodium salt shows violet fluorescence.

Reactions.—It couples with diazotised bases forming *azo*-dyes. Its *diazo*- compound is only sparingly soluble. Digestion with 60 p.c. caustic soda solution at 230°–280° converts it into *o-toluic acid* (Kalle, D. R.-P. 79028; Eng. P. 16559 of 1894).

(iii.) β-**Naphthylamine-5-sulphonic acid** (γ-*acid; Dahl acid*), mixed with the 8-sulphonic acid, has been stated to form about 40 p.c. of the product obtained when β-naphthylamine is heated with 3 times its weight of sulphuric acid at 100°–105°, or about 55 p.c. of that obtained when β-naphthylamine sulphate is sulphonated at 15°–20° with 3 times its weight of sulphuric acid (Dahl, D. R.-P. 32276), or 68–70 p.c. of that obtained when β-naphthylamine is sulphonated with 3 times its weight of 20 p.c. anhydro-acid at 70°–80° (Dahl, D. R.-P. 29084; Eng. P. 7712 of 1884). According to Green and Vakil, it constitutes 55–60 p.c. of the product formed when β-naphthylamine is sulphonated with sulphuric acid (4 pts.) or 20 p.c. anhydro-acid (3 pts.) at 20°–80° during 5 hours (Chem. Soc. Trans. 1918, 113, 38; *v.* p. 413). It is also obtained when acetyl-β-naphthylamine is sulphonated at 20°–30° with 5 times its weight of sulphuric acid, and the product de-acetylated by boiling it with water (Kinzlberger, D. P. Anm. K. 5732).

Preparation.—β-Naphthylamine sulphate (85 pts.) is stirred with sulphuric acid (270 pts.) at 15°–20° during 48–70 hours until sulphonated, the product then poured into water, the precipitated acids converted into sodium salt, and the dry sodium salt extracted by boiling 90–95 p.c. alcohol, in which the 8-sulphonate is insoluble. The residue left after removal of the alcohol from the filtrate by distillation, is dissolved in water; the acids precipitated by hydrochloric acid are converted into barium salt, and this crystallised fractionally to separate the sparingly soluble 6- and 7-sulphonates which may be present in small quantity. A partial separation can be effected previous to the extraction with alcohol by converting the sulphonation product into the barium or calcium salt, and allowing the 6-, 7-, and 8-sulphonates to separate, as far as possible, from the concentrated solution (Dahl, D. R.-P. 32271, 32276).

Identification.—The *acid* HA forms needles or scales, soluble in 260 parts of boiling or 1300 parts of cold water. The salts dissolve easily in water, and, like the acid, show reddish-blue fluorescence in dilute solution. The *barium* salt $BaA_2+2\frac{1}{2}H_2O$ forms granular aggregates; the *calcium* salt CaA_2+11H_2O, needles, soluble in 11 parts of cold water; the *potassium* salt KA+H_2O, small rhombohedra; the *sodium* salt NaA+5H_2O, prisms, soluble in 10 parts of boiling 95 p.c. alcohol; the *ammonium* salt, plates (*cf.* Forsling, Ber. 1887, 20, 2103). It is convertible into *β-chloronaphthalene-5-sulphonyl*

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[1] In every case where the constitution of a β-naphthylaminesulphonic acid is given, the NH_2 group is supposed to be in the position '2.'

chloride, prisms, m.p. 70°, and 1 : 6-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 48; Cleve, Ber. 1892, 25, 2481; Forsling, *l.c.*).

Reactions.—From its sparingly soluble *diazo*-compound, *β-naphthol-5-sulphonic acid* has been obtained. Fusion with caustic potash at 260°–270° converts it into 2-*amino-5-naphthol*. On sulphonation with 20 p.c. anhydro-acid in the cold it yields a mixture of *β-naphthylamine*-5 : 7-*disulphonic acid* with the 1 : 5-*disulphonic acid* as minor product.

(iv.) β-**Naphthylamine-6-sulphonic acid** ([β-] *acid*; *Brönner acid*) occurs to the extent of about 50 p.c. in the product formed when β-naphthylamine sulphate, or β-naphthylamine-5- or 8-sulphonic acid is heated with 3 times its weight of sulphuric acid at 160°–170° for 2 hours (*v.* 7-sulphonic acid). It is also produced, mixed with a small proportion of the 7-sulphonic acid (Bayer and Duisberg, Ber. 1887, 20, 1429), when β-naphthylamine hydrogen sulphate is baked at 200°–210° for 2 hours (Liebmann, D. P. Anm. L 3205); or when β-naphthylamine is heated with 3 times its weight of potassium bisulphate at about 230° (Bischoff and Brodsky, Ber. 1890, 23, 1914).

Preparation.—β-Naphthylamine-6-sulphonic acid and its salts, being much less soluble in water than the 7- compounds, can be separated without much difficulty by fractional crystallisation from the products obtained either by sulphonating β-naphthylamine under the conditions just described, or by heating impure β-naphthol-6-sulphonic acid, containing the 7-isomeride, with ammonia (*cf.* Green, Chem. Soc. Trans. 1889, 55, 37; Eng. P. 15849 of 1888). As with the 7-isomeride, the purity of the 6-sulphonic acid can be judged from the appearance of its crystals, or of those of its ammonium salt, as they separate from solution (Green, *l.c.*).

The pure acid[1] is obtained when β-naphthol-6-sulphonic acid is heated with aqueous ammonia at 180° under pressure (Brönner, D. R.-P. 22547; Eng. P. 3724 of 1882; *cf.* Landshoff, D. R.-P. 27378; Ber. 1883, 16, 1932); or, much more easily, when the bisulphite method is applied to it (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357; Badische, D. R.-P. 115335, 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Identification.—The *acid* $HA+H_2O$ crystallises in scales, soluble in 630 parts of boiling water (Weinberg, Ber. 1887, 20, 2909), and, like its salts, shows blue fluorescence in solution. The *lead* salt PbA_2+2H_2O forms scales, soluble in 670 parts of water at 1°; the *barium* salt BaA_2+6H_2O, long needles, soluble in 450 parts of cold water; the *calcium* salt CaA_2+6H_2O, scales, soluble in 225 parts of water at 5°; the *potassium* salt $KA+H_2O$, silky needles, soluble in 40–45 parts of cold water; the *sodium* salt $NaA+2H_2O$, silky needles, soluble in about 40 parts of cold water, and easily in hot 90 p.c. alcohol (*cf.* Forsling, Ber. 1887, 20, 77; Limpricht, quoted by Schultz, Chemie des Steinkohlenth., 3rd ed. i. 209). The *ammonium* salt NH_4A+H_2O, large thin plates, is the least soluble of the ammonium β-naphthylamine-sulphonates in cold water (Green, *l.c.*). It is convertible into *β-chloronaphthalene-6-sulphonyl chloride*, prisms, m.p. 109° (Forsling, *l.c.*), and 2 : 6-*dichloronaphthalene* (Forsling, *l.c.*; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 52).

Reactions.—It couples with diazotised bases forming the end component of some *disazo*- dyes. From its moderately soluble yellow *diazo*-compound or by the bisulphite method, *β-naphthol-6-sulphonic acid* can be obtained. On sulphonation with 20 p.c. anhydro-acid at 20°, it yields a mixture of *β-naphthylamine*-1 : 6-*disulphonic acid* with about 20 p.c. of the 6 : 8-*disulphonic acid*.

Substitution derivatives in which methyl, phenyl and fuchsin radicles respectively occur in the amino- group of β-naphthylamine-6-sulphonic acid can be obtained by the bisulphite method if methylamine, aniline and fuchsin are used in place of ammonia (Badische, D. R.-P. 121683, 122570, 125589; Eng. P. 18726 of 1900).

(v.) β-**Naphthylamine-7-sulphonic acid** ([δ-] *acid*; F-*acid*) is obtained, mixed with about an equal quantity of the 6-sulphonic acid (Schultz, Ber. 1887, 20, 3159), when β-naphthylamine is heated with 6 times its weight of sulphuric acid at temperatures above 150° (Bayer, D. R.-P. 39925; Eng. P. 5846 of 1886); when β-naphthylamine sulphate is heated with 3 times its weight of sulphuric acid at 160°–170° (Bayer, D. R.-P. 41505); or when β-naphthylamine-5- or 8-sulphonic acid is heated with 3 times its weight of sulphuric acid at 160°–170° for about 2 hours (Bayer, D. R.-P. 42272, 42273; Weinberg, Ber. 1887, 20, 3354; Erdmann, Ber. 1888, 21, 637). It is also said to be the product when acetyl-β-naphthylamine is heated with 6 times its weight of sulphuric acid at 150°–160° for 1–1½ hours, and the product de-acetylated by pouring the hot melt into water (Kinzlberger, D. P. Anm. K. 5732).

Preparation.—From the mixture of acids precipitated by pouring the sulphonation melt obtained from β-naphthylamine at 160°–170° on to ice the 6-sulphonic acid can be isolated with little trouble, but the separation of pure 7-sulphonic acid is much more difficult. Fractional crystallisation of the mixed acids from water at about 80° (Schultz, Ber. 1887, 20, 3159), or of the mixed copper salts (Aktienges., D. R.-P. 44248; Eng. P. 687 of 1888), or lead salts (Aktienges., D. R.-P. 44249; Eng. P. *l.c.*), the 7-compound being in each case the more soluble, can be employed in the laboratory but is valueless on the large scale. The purity of the 7-sulphonic acid isolated by any of these methods can be judged from the appearance of its crystals or of those of its ammonium salt as they separate from solution (Green, Chem. Soc. Trans. 1889, 55, 36).

The pure acid is obtained when sodium β-naphthol-7-sulphonate is heated with twice its weight of 20 p.c. ammonia at 250° for 6 hours under pressure (Cassella, D. R.-P. 43740; Eng. P. 12908 of 1886; Bayer and Duisberg, Ber. 1887, 20, 1432; Weinberg, *ibid.* 2908); or more easily when the bisulphite method is applied to it (Bucherer, J. pr. Chem. 1904, [ii.] 70, 357;

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[1] The second naphthylaminesulphonic acid—characterised by its solubility in water, the solubility of its sodium salt in alcohol, and the redder shade of the derived azo-dyes—which is stated by the Farbfabrik vorm. Bronner (*l.c.*) to occur in the Bronner product, doubtless owed its origin to impurity in the Schäffer acid employed (*cf.* Bayer and Duisberg, Ber. 1887, 20, 1427).

Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Identification.—The *acid* $HA+H_2O$ forms slender, voluminous needles soluble in 350 parts of boiling water. When boiled with a quantity of water insufficient to dissolve it, the crystalline acid changes into a very sparingly soluble, anhydrous, sandy powder. The *barium* salt BaA_2+5H_2O forms thin scales, soluble in 400 parts of cold water; the *calcium* salt CaA_2+6H_2O, scales, soluble in 270 parts of cold water; the *potassium* salt, needles, soluble in 40 parts of cold water; the *ammonium* salt, small plates; the *sodium* salt $NaA+4H_2O$, small needles, soluble in hot 90 p.c. alcohol and in 70 parts of cold water (*cf.* Bayer and Duisberg, *l.c.*; Weinberg, *l.c.*; Schultz, *l.c.*). The solutions of the salts show reddish-violet fluorescence. It is convertible into *β-chloronaphthalene-7-sulphonyl chloride*, prisms, m.p. 86° (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 49; Cleve, Ber. 1892, 25, 2484), and 2:7-*dichloronaphthalene* (Erdmann, Ber. 1888, 21, 638; Armstrong and Wynne, *l.c.*).

Reactions.—It couples with diazotised bases, being end component of some *disazo-* dyes. From its orange-red *diazo-* compound or by the bisulphite method *β-naphthol-7-sulphonic acid* can be obtained. Digestion with 50 p.c. caustic soda solution at 260°–280° converts it into 2-*amino-7-naphthol.* Heated with 20 p.c. sodium bisulphite solution at 90°-100° for 24 hours, its sodium salt is converted into sodium *ββ′-dinaphthylamine-7:7′-disulphonate.* On sulphonation with 20–25 p.c. anhydro-acid at the ordinary temperature, it yields three *β-naphthylaminedisulphonic acids, viz.* the 1:7-, 4:7-, and 5:7-isomerides.

The *dimethyl-* derivative, obtained by heating the acid with dimethylamine under pressure at 220°, is converted into *dimethyl-2-amino-7-naphthol* by fusion with caustic alkali (Geigy. D. R.-P. 90310).

(vi.) β-**Naphthylamine**-8-**sulphonic acid** ([*a*-] *acid; Badische acid*) is formed (39–44 p.c.), together with the 5-sulphonic acid and about 1 p.c. of the mixed 6- and 7-isomerides, when β-naphthylamine is heated with 3 times its weight of sulphuric acid at 100°-105°[1] for about 6 hours (Badische, D. R.-P. 20760; Dahl, D. R.-P. 29084, Eng. P. 7712 of 1884; Green and Vakil, Chem. Soc. Trans. 1918, 113, 38; *cf.* Green, *ibid.* 1889, 55, 36). The proportion of the 8-sulphonic acid does not exceed 45 p.c. when β-naphthylamine sulphate is sulphonated with 3 times its weight of sulphuric acid at 15°–20°, while it amounts only to 30 p.c. when β-naphthylamine is sulphonated with 3 times its weight of 20 p.c. anhydro-acid at 70°–80° (Dahl, *l.c.*; Green, *l.c.*). The acid is also obtained when β-naphthol-8-sulphonic acid is heated with ammonia under pressure (Bayer, D. R.-P. 42273; Pfitzinger and Duisberg, Ber. 1889, 22, 397), or when the bisulphite reaction is applied to it (Bucherer, J. pr. Chem. 1904, [ii.] 70, 358; Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Preparation.—The product obtained by sulphonating β-naphthylamine sulphate with 3 times its weight of sulphuric acid at 15°-20° is converted into sodium salt, which, as a dry powder, is extracted with 90–95 p.c. alcohol to remove the isomeric salts, the residue consisting of the pure sodium β-naphthylamine-8-sulphonate (Dahl, *l.c.*; Green, *l.c.*; *v.* 5-sulphonic acid).

Identification.—The *acid* forms slender needles, soluble in 200 parts of boiling or in 1700 parts of cold water. The salts, like the acid, show blue fluorescence in dilute solution (*cf.* Forsling, Ber. 1887, 20, 2100). The *barium* salt BaA_2+4H_2O forms prisms, soluble in 23 parts of cold water; the *calcium* salt CaA_2+6H_2O, prisms, soluble in 11 parts of cold water; the *potassium* salt $KA+\frac{1}{2}H_2O$, six-sided prisms; the *sodium* salt NaA (Erdmann, Annalen, 1893, 275, 281), large prisms, insoluble in alcohol; the *ammonium* salt (Green, *l.c.*), large solid prisms. It is convertible into *β-chloronaphthalene-8-sulphonyl chloride*, needles, m.p. 129°, and 1:7-*dichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1888, 4, 105; 1889, 5, 53; Forsling, *l.c.*; Ber. 1888, 21, 2803; 1889, 22, 619).

Reactions.—It does not furnish azo-dyes by coupling with diazotised bases, but soluble yellow *diazo-amino-* compounds (Witt, Ber. 1888, 21, 3483; Erdmann, *l.c.*). From its sparingly soluble *diazo-* compound or by the bisulphite method, *β-naphthol-8-sulphonic acid* can be obtained. Fusion with caustic alkali at 260°–270° converts it into 2-*amino-8-naphthol.* On sulphonation in the cold with 20 p.c. anhydro-acid, it gives *β-naphthylamine-6:8-disulphonic acid.*

β-Naphthylaminedisulphonic Acids.

(i.) β-**Naphthylamine**-1:5-**disulphonic acid** is obtained when β-naphthylamine-1-sulphonic acid is sulphonated with 20 p.c. anhydro-acid in the cold (Armstrong and Wynne, Chem. Soc. Proc. 1895, 11, 238); *or* (as minor product) mixed with the 5:7-disulphonic acid when β-naphthylamine-5-sulphonic acid is sulphonated under similar conditions (Armstrong and Wynne, *ibid.* 1890, 6, 129).

Identification.—The *normal potassium* salt is moderately soluble in water, and convertible into *β-chloronaphthalene-1:5-disulphonyl chloride*, prisms, m.p. 158°, and 1:2:5-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—From its sparingly soluble *diazo-* compound, the *diazo-oxide* of 2-amino-1-naphthol-5-sulphonic acid is obtained either by addition of sodium carbonate at 50°–60° to remove free mineral acid, or by oxidation with sodium hypochlorite in alkaline solution (Badische, D. R.-P. 145906; Eng. P. 6615 of 1902; D. R.-P. 160536; Eng. P. 4997 of 1904). Fusion with caustic alkali at 210°–230° converts it into 2-*amino-5-naphthol-1-sulphonic acid.* On sulphonation with 40 p.c. anhydro-acid at 100°, it yields *β-naphthylamine-1:5:7-trisulphonic acid.*

(ii.) β-**Naphthylamine**-1:6-**disulphonic acid** is obtained as chief product, with about 20 p.c.

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[1] Forsling's statement that the sulphonation product at 140° consists almost entirely of a mixture of the 5- and 8-sulphonic acids (Ber. 1887, 20, 2100) must be regarded as incorrect in view of the fact that the product at 120° contains no less than 7·5 p.c. of the mixed 6- and 7-sulphonic acids (Green and Vakil, *l.c.*; *cf.* Bayer, D. R.-P. 42273; Weinberg, Ber. 1887, 20, 3354).

of the 6 : 8-disulphonic acid, when β-naphthylamine-6-sulphonic acid is sulphonated with 20 p.c. anhydro-acid at a temperature below 20° (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 130; *cf.* Forsling, Ber. 1888, 21, 3495); *or*, pure, by applying the bisulphite reaction to sodium β-naphthol-1 : 6-disulphonate (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Identification.—The *normal potassium* salt K_2A+2H_2O in large crystals, the *sodium* salt in long needles, and the *ammonium* salt $(NH_4)_2A+H_2O$ in triclinic forms, are very soluble; but the *acid potassium* salt $KHA+H_2O$ and *acid sodium* salt $NaHA+2H_2O$, in long needles, are only sparingly so, and in dilute solution show blue fluorescence (Forsling, *l.c.*). It is convertible into *β-chloronaphthalene*-1 : 6-*disulphonyl chloride*, prisms, m p. 124 5°, and 1 : 2 · 6-*trichloronaphthalene* (Forsling, *l.c* ; Armstrong and Wynne, *l.c.*).

Reaction.—Its sparingly soluble, crystalline *diazo-* compound, when warmed with excess of sodium carbonate solution, yields the *diazo-oxide* of 2-amino-1-naphthol-6-sulphonic acid (Badische, D. R.-P. 148882; Eng. P. 6615 of 1902).

(iii.) β-**Naphthylamine**-1 : 7-**disulphonic acid,** formed (25 p.c.), together with the 4 : 7- and 5 : 7-disulphonic acids, when β-naphthylamine-7-sulphonic acid is sulphonated in the cold with 20–25 p c. anhydro-acid, is separated from the product by converting it into normal potassium salt, and collecting the least soluble portion by fractional crystallisation (Bayer, D. R.-P 79243; Dressel and Kothe, Ber. 1894, 27, 1194) It is also obtained when potassium β-naphthol-1 : 7-disulphonate is heated either with ammonium chloride and ammonia solution at 180°-200° (Bayer, D P. Anm. F 7274, D. R.-P. 77596; Eng. P. 1063 of 1894; Dressel and Kothe, *l.c.* 1206), or more easily when the bisulphite method is applied to it (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416).

Identification.—The *normal barium* salt, moderately soluble needles, the *potassium* salt K_2A+3H_2O, large monosymmetric crystals, and the *acid potassium* salt, sparingly soluble slender needles, give solutions showing violet-blue fluorescence (Dressel and Kothe, *l c.*).

Reactions.—In acetic acid solution it does not couple with diazobenzene (Bayer, D. P. Anm. F. 7274). From its easily soluble *diazo-* compound, *β-naphthol*-1 : 7-*disulphonic acid* can be obtained, and, when warmed with sodium carbonate solution, the *diazo-oxide* of 2-amino-1-naphthol-7-sulphonic acid (Badische, D. R.-P. 148882; Eng. P. 6615 of 1902). Prolonged boiling with 20 p.c. hydrochloric acid converts it into *β-naphthylamine-7-sulphonic acid* (Dressel and Kothe, *l.c.*).

(iv.) β-**Naphthylamine**-3 : 6-**disulphonic acid** (*β-naphthylamine-[α-]disulphonic acid; amino-R-acid*) is obtained from sodium β-naphthol 3 : 6-disulphonate either by heating it with ammonia at 200°-250° under pressure (Pfitzinger and Duisberg, Ber. 1889, 22, 398, *cf.* Landshoff, D. R.-P. 27378); or more easily by the application of the bisulphite method (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416). It is also formed when sodium β-naphthylamine-3 : 6 : 8-trisulphonate is boiled with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934). It is convertible into *β-chloronaphthalene*-3 : 6-*disulphonyl chloride*, needles, m.p. 165°, and 2 : 3 · 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 12).

Reactions—It couples with diazotised bases as end component in numerous *monoazo-* and *disazo*-dyes Digestion with 75 p.c. caustic soda solution at 230°-250° converts it into *2-amino-3-naphthol-6-sulphonic acid.*

(v.) β-**Naphthylamine**-3 : 7 **disulphonic acid** (*β-naphthylamine-*[δ-]*disulphonic acid*), formed when sodium β-naphthol-3 . 7-disulphonate is heated with 25 p.c. ammonia solution under pressure at 200° (Cassella, D. R.-P. 46711), is more easily obtained when the bisulphite method is applied to it (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p 416). It is also obtained when β-naphthylamine-1 · 3 : 7-trisulphonic acid is boiled with dilute mineral acids (Dressel and Kothe, Ber. 1894, 27, 1199).

Identification—The *acid barium* salt forms very sparingly soluble microscopic crystals; the *acid potassium* salt, sparingly soluble scales; the *acid sodium* salt dissolves in 12·5 parts of boiling water, or in 50 parts of water at 20°, the solutions showing blue fluorescence (Dressel and Kothe, *l c.*) It is convertible into *β-chloronaphthalene*-3 : 7-*disulphonyl chloride*, needles, m p. 176°, and 2 . 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc Proc. 1890, 6, 127).

Reactions.—It couples with diazotised bases as end component in *disazo-* dyes. On sulphonation with 40 p c anhydro acid at 80°–90°, it is converted into *β-naphthylamine*-1 : 3 : 7-*trisulphonic acid.*

(vi.) β-**Naphthylamine**-4 : 7-**disulphonic acid** (*Andresen's acid*) is obtained when β-nitronaphthalene-4 . 7-disulphonic acid is reduced (Schultz, Ber. 1890, 23, 77), *or* (25 p.c.) when β-naphthylamine-7-sulphonic acid is sulphonated with 20–25 p.c. anhydro-acid in the cold, and, after removal of the 1 : 7-disulphonic acid as potassium salt, is separated as normal sodium salt from the more soluble 5 : 7-disulphonate (Bayer, D. R.-P. 79243; Dressel and Kothe, Ber. 1894, 27, 1196; *v.* 5 : 7-disulphonic acid).

Identification.—The normal *barium* and *sodium* salts, crystalline crusts, and the *acid sodium* salt $NaHA+H_2O$, needles, in dilute solution show intense blue fluorescence (Dressel and Kothe, *l.c.*). It is convertible into *β-chloronaphthalene*-4 : 7-*disulphonyl chloride*, needles, m.p. 174°, and 1 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1891, 7, 27).

Reactions.—Diazotised it furnishes *β-naphthol*-4 : 7-*disulphonic acid* when boiled with water. Digestion with 35 p.c. caustic potash solution at 180°-200° converts it into 2-*amino*-4-*naphthol*-7-*sulphonic acid.* When heated with aniline and aniline hydrochloride at 150°-170° it yields *diphenyl*-1 : 3-*diaminonaphthalene*-6-*sulphonic acid.*

(vii.) β-**Naphthylamine**-4 : 8-**disulphonic acid** (*C-acid*) is obtained by the reduction of β-nitronaphthalene-4 : 8-disulphonic acid (Cassella, D. R.-P. 65997; Fischer, *cf.* J. Soc. Chem. Ind. 1898, 17, 837).

Identification.—The *acid* forms prisms; the *acid barium* salt BaH_2A_2, minute needles; the *acid sodium* salt, needles, easily soluble in hot water. The alkaline solutions show deep blue fluorescence. It is convertible into *naphthalene-1 : 5-disulphonic acid* (Cassella, *l.c.*).

Reactions.—It does not couple with diazotised bases (Cassella, *l.c.*). From its moderately soluble *diazo-* compound, *β-naphthol*-4 : 8-*disulphonic acid* has been obtained. Fusion with caustic alkali at 215° converts it into 2-*amino*-4-*naphthol-8-sulphonic acid*. By digestion with water or 10 p.c. sulphuric acid at 180°, it yields *β-naphthol-4-sulphonic acid.*

When boiled with zinc-dust and dilute caustic soda solution it furnishes a mixture of the *β-naphthylamine*-4- and 8-*sulphonic acids* (Kalle, D. R.-P. 233934), but with sodium amalgam in the cold the products are *β-naphthylamine-8-sulphonic acid* (Bayer, D. R.-P. 255724, Eng. P. 28172 of 1911) and *β-naphthylamine* (Friedlander and Lucht, Ber. 1893, 26, 3033). Nitration converts its acetyl derivative into the 6-*nitro-* compound (Höchst, D. P. Anm. F. 31417). When heated with aniline and aniline hydrochloride at 150–170° it yields *diphenyl*-1 : 3-*diaminonaphthalene-5-sulphonic acid.* By sulphonation with 40 p.c. anhydro-acid at 80°–120°, *β-naphthylamine*-4 : 6 . 8-*trisulphonic acid* is obtained.

(viii.) *β*-**Naphthylamine-5 : 7-disulphonic acid** is obtained as chief product, mixed either with 1 : 5-disulphonic acid when *β*-naphthylamine-5-sulphonic acid, or with the 1 : 7- and 4 : 7-disulphonic acids when *β*-naphthylamine-7-sulphonic acid is sulphonated with 4 times its weight of 20 p.c. anhydro-acid at the ordinary temperature. About five days are required for the former and about two for the latter process. In both cases the melt, after dilution with water, is neutralised by lime and converted into potassium salt.

Separation.—(*a*) From the concentrated solution of the mixed normal potassium salts, the 1 : 5-disulphonate can be removed by crystallisation, the acid potassium salt of the 5 : 7-disulphonic acid being obtained from the mother liquor by acidifying it with hydrochloric acid (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 129).

(*b*) From the solution of the mixed normal potassium salts, concentrated to 6 litres for each 2 kilos. of the 7-sulphonic acid used, the 1 : 7-disulphonate separates in large crystals and is removed by filtration. The filtrate, acidified by hydrochloric acid, furnishes the acid potassium salts of the 4 : 7- and 5 : 7-disulphonic acids, which collected, dissolved in hot water, precipitated as acid barium salts by adding barium chloride (1·1 kilos.) in hot concentrated solution and the precipitate digested with sodium carbonate, are converted into normal sodium salts and the resulting solution concentrated to about 2·5 litres. Eventually the whole of the 4 : 7-disulphonic acid separates as normal sodium salt and is collected while the filtrate on acidification yields the acid sodium salt of the 5 : 7-disulphonic acid (Bayer, D. R.-P. 79243; Dressel and Kothe, Ber. 1894, 27, 1197; *cf.* Armstrong and Wynne, *l.c.* 131).

Identification.—The *acid potassium* salt is easily soluble, and convertible into *β-chloronaphthalene*-5 : 7-*disulphonyl chloride*, prisms, m.p. 156°; and 1 : 3 : 6-*trichloronaphthalene* (Armstrong and Wynne, *l.c.*).

Reactions.—By the bisulphite method, it furnishes *β-naphthol*-5 : 7-*disulphonic acid.* Digestion with 50 p.c. caustic soda solution at 190° converts it into 2-*amino-5-naphthol-7-sulphonic acid* (J-acid). On sulphonation with 40 p.c. anhydro-acid at 100°, it yields *β-naphthylamine-1 : 5 : 7-trisulphonic acid.* When desulphonated by sodium amalgam in the cold, *β-naphthylamine-7-sulphonic acid* is the product (Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911).

Converted into the toluene *p*-sulphonyl derivative, it gives the 1-*chloro*-compound on chlorination, from which 1-*chloro-2-amino-5-naphthol-7-sulphonic acid* can be prepared.

(ix.) *β*-**Naphthylamine-6 : 8-disulphonic acid** (*β-naphthylamine-[γ-]disulphonic acid; amino-G-acid*) is formed as chief product when *β*-naphthylamine sulphate is heated with three times its weight of 20–30 p.c. anhydro-acid at 110°–140° until a test dissolves completely in water, *or* when crude *β*-naphthylamine-8-sulphonic acid is heated with 10 p.c. anhydro-acid at 100° (Gans & Co., D. R.-P. 35019; Eng. P. 816 of 1884); also as chief product when *β*-naphthylamine-8-sulphonic acid is sulphonated with 20 p.c. anhydro-acid below 20° (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 128), *or* as minor product (20 p.c.) when the 6-sulphonic acid is sulphonated with 20 p.c. anhydro-acid below 20° (Armstrong and Wynne, *ibid.* 130).

Preparation.—The pure acid is obtained from sodium *β*-naphthol 6 . 8-disulphonate either by heating it with ammonia at 200° under pressure (*cf.* Landshoff, D. R.-P. 27378), or more easily when the bisulphite method is applied to it (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 70, 358; *v.* p. 416).

Identification.—The acid and salts are easily soluble. It is convertible into *β-chloronaphthalene-6 : 8-disulphonyl chloride*, needles, m.p. 170°, and 1 . 3 : 7-*trichloronaphthalene* (Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 13).

Reactions.—It does not couple with diazotised bases (*cf.* Witt, Ber. 1888, 21, 3487). Digestion with 75 p.c. caustic soda solution at 230°–250° converts it into 2-*amino-8-naphthol-6-sulphonic acid*, but at 270°–280° into *hydroxytoluic acid* (Hochst, D. R.-P. 81281). On sulphonation with 40 p.c. anhydro-acid at 80°–90°, it yields *β-naphthylsulphamino*-6 : 8-*disulphonic acid* (Dressel and Kothe, Ber. 1984, 27, 2153), but at 120°–130°, *β-naphthylamine*-3 : 6 : 8-*trisulphonic acid.*

β-NAPHTHYLAMINETRISULPHONIC ACIDS.

(i.) *β*-**Naphthylamine-1 : 3 : 7-trisulphonic acid** is formed when *β*-naphthylamine-3 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 80°–90° (Bayer, D. P. Anm. F. 7036; Dressel and Kothe, Ber. 1894, 27, 1199); also when *β*-naphthol-1 : 3 : 7-trisulphonic acid is heated with 25 p.c. ammonia solution under pressure at 190° (Bayer, D. P. Anm. F. 7003; Eng. P. 17141 of 1893; Dressel and Kothe, *l.c.*). The *acid barium* salt and *acid sodium* salt Na_2HA+4H_2O in scales, are easily soluble, and in solution show violet-blue fluorescence.

Reactions.—When boiled with dilute mineral acid it yields *β-naphthylamine*-3 : 7-*disulphonic acid.* On sulphonation with 40 p.c. anhydro-acid at 130° it is converted into a mixture of the 3 : 5 : 7- and 3 : 6 : 7-*trisulphonic acids* with the 1 : 3 : 6 : 7-*tetrasulphonic acid.*

(ii.) β - **Naphthylamine** - 1 : 5 : 7 - **trisulphonic acid** is formed when β-naphthylamine-5-sulphonic, or 1 : 5-disulphonic, or 5 : 7-disulphonic acid is sulphonated with 40 p.c. anhydro-acid at 100° (Bayer, D. R.-P. 80878 ; Eng. P. 20580 of 1893). The *barium, acid potassium* and *acid sodium* salts dissolve easily, giving solutions which show blue fluorescence.

Reactions.—It does not couple with diazobenzene chloride (Bayer, *l.c.*). From its easily soluble *diazo*-compound, the *diazo-oxide* of 2-amino-1-naphthol-5 : 7-disulphonic acid is obtained when the solution is rendered alkaline by sodium carbonate (Höchst, D. P. Anm. F. 16863 ; Eng. P. 23993 of 1902). Digestion with 65 p.c. caustic soda solution at 160°–220° converts it into 2-*amino-5-naphthol*-1 : 7-*disulphonic acid.* By partial hydrolysis with boiling dilute mineral acids it yields *β-naphthylamine*-5 : 7-*disulphonic acid.* When heated with 30 p.c. anhydro-acid at 140°–160° it undergoes change into the isomeric *β-naphthylamine* - 3 : 5 : 7-*trisulphonic acid.*

(iii.) β-**Naphthylamine** - 3 : 5 : 7 - **trisulphonic acid** is formed, together with the 3 : 6 : 7-trisulphonic and the 1 : 3 : 6 : 7-tetrasulphonic acids, when β-naphthylamine-3 : 7-disulphonic acid is heated with 40 p.c. anhydro-acid at 130°. By boiling the product with water, the tetrasulphonic acid is hydrolysed to the 3 : 6 : 7-trisulphonic acid, which is then converted into sodium salt, and, after acidification, separated as the sparingly soluble acid sodium salt. From the concentrated mother liquor, the easily soluble acid sodium salt of the 3 : 5 : 7-isomeride can be separated (Bayer, D. R.-P. 81762 ; Eng P. 17141A of 1893 ; Dressel and Kothe, Ber. 1894, 27, 1202). It is the sole product of the change which occurs when β-naphthylamine-1 : 5 : 7-trisulphonic acid is heated with 30 p.c. anhydro-acid at 140°–160° (Bayer, D. R.-P. 90849).

Identification.—The *sodium* salt $(+5\frac{1}{2}H_2O)$ from dilute alcohol, the *acid sodium* salt Na_2HA, and the *acid barium* salt are very soluble, and in solution show intense green fluorescence. It is convertible into *naphthalene*-1 : 3 : 7-*trisulphonic acid* (Dressel and Kothe, *ibid.* 1203).

Reactions.—From its very soluble *diazo*-compound, *β-naphthol*-3 : 5 : 7-*trisulphonic acid* has been obtained (Dressel and Kothe, *l.c.*). Digestion with 30 p.c. caustic soda solution at 190° converts it into 2-*amino-5-naphthol*-3 : 7-*disulphonic acid.*

(iv.) β - **Naphthylamine** - 3 : 6 : 7 - **trisulphonic acid** is formed when β-naphthylamine-3 : 7-disulphonic acid is heated with 40 p.c. anhydro-acid at 130°, being separated by means of its sparingly soluble acid sodium salt from the 3 : 5 : 7-trisulphonic acid also produced (*q.v.*); *or* when β naphthylamine-1 : 3 : 6 : 7-tetrasulphonic acid is boiled with dilute mineral acids (Bayer, D. R.-P. 81762 ; Eng. P. 17141A of 1893); *or* when β-naphthol-3 : 6 : 7 trisulphonic acid is heated with 25 p.c. ammonia solution (3 pts.) and ammonium chloride (0·5 pt.) during 8 hours at 30–40 atmos. pressure (Bayer, D. P. Anm. F. 7019 ; Eng. P. 17141 of 1893).

Identification.—The *sodium* salt is easily, the *barium* salt and *acid sodium* salt Na_2HA+3H_2O in long silky needles are sparingly soluble in cold water, the solutions showing intense blue fluorescence. It is convertible into *naphthalene*-2 : 3 : 6-*trisulphonic acid* (Dressel and Kothe, Ber. 1894, 27, 1202).

Reactions.—From its sparingly soluble *diazo*-compound *β-naphthol*-3 : 6 : 7-*trisulphonic acid* has been obtained. Digestion with 55 p.c. caustic soda solution at 180°–240° converts it into 2-*amino-7-naphthol*-3 : 6-*disulphonic acid.* On sulphonation with 40 p.c. anhydro-acid at 100°–130°, it yields *β-naphthylamine*-1 : 3 : 6 : 7-*tetrasulphonic acid.*

(v.) β - **Naphthylamine** - 3 : 6 : 8 - **trisulphonic acid** is obtained when β-naphthol-3 : 6 : 8-trisulphonic acid is heated with ammonia at 200°–250° (Landshoff, D. R.-P. 27378 ; *cf.* Dressel and Kothe, Ber. 1894, 27, 2154); *or* when β-naphthylamine-6 : 8-disulphonic acid is heated with 40 p.c. anhydro-acid at 120°–130° (Dressel and Kothe, *l.c.*); *or* when sodium α-nitronaphthalene-3 : 6 : 8-trisulphonate is heated with ammonia solution under pressure at 150°–170°, nitrogen being eliminated (Kalle, D. R.-P. 176621).

Identification.—The *acid potassium* salt $K_2HA+1\frac{1}{2}H_2O$ forms needles, soluble in 40 parts of water at 20° ; the *acid sodium* salt, easily soluble needles ; the solutions show intense sky-blue fluorescence. It is convertible into *naphthalene*-1 : 3 : 6 *trisulphonic acid* (Dressel and Kothe, *l.c.*).

Reactions.—Digestion with 80 p.c. caustic soda solution at 220°–260° converts it into 2-*amino-8-naphthol*-3 : 6-*disulphonic acid.* By desulphonation with zinc-dust and boiling dilute caustic soda solution, it yields *β-naphthylamine*-3 : 6-*disulphonic acid.*

(vi.) β - **Naphthylamine** - 4 : 6 : 8 - **trisulphonic acid** is obtained when sodium β-naphthylamine-4 : 8-disulphonate is heated with 40 p.c. anhydro-acid at 80°–90°, and finally at 120°.

Reaction.—When heated with 60 p.c. caustic soda solution at 170°–180°, it is converted into 2-*amino-4-naphthol*-6 : 8-*disulphonic acid* (Bayer, D. P. Anm. F. 8154 ; D. R.-P. 89242).

β-NAPHTHYLAMINETETRASULPHONIC ACID.

β-**Naphthylamine**-1 : 3 : 6 : **7-tetrasulphonic acid** occurs in the product formed when β-naphthylamine-3 : 7-disulphonic acid is heated with 40 p.c. anhydro-acid at 130° (*v.* 3 : 5 : 7-trisulphonic acid). It is obtained when β-naphthylamine-3 : 6 : 7-trisulphonic acid is heated with 40 p.c anhydro-acid at 100°–130° (Dressel and Kothe, Ber. 1894, 27, 1203), *or* when sodium β-naphthol-1 : 3 : 6 : 7-tetrasulphonate is heated with 25 p.c. ammonia solution at 180° under pressure (Bayer, D. P. Anm. F. 7003 ; Eng. P. 17141 of 1893 ; Dressel and Kothe, *l.c.*).

Salts.—The *barium* salt Ba_2A+6H_2O, in sparingly soluble, microscopic crystals, and the easily soluble *sodium* salt show, in dilute solution, violet-blue fluorescence. Acid salts have not been obtained, and acid solutions when boiled undergo partial hydrolysis, giving rise to *β-naphthylamine*-3 : 6 : 7-*trisulphonic acid.*

Chloro-β-naphthylamine.

1-Chloro-β-naphthylamine obtained by chlorinating acetyl-β-naphthylamine, in acetic acid solution, and hydrolysing the product with hot hydrochloric acid, forms needles, m.p. 59°, and is convertible into 1 : 2-*dichloronaphthalene*. The *hydrochloride* B·HCl+H_2O forms needles; the *acetyl* derivative, needles, m.p. 147° (Cleve, Ber. 1887, 20, 1989).

1-Chloro-β-naphthylaminesulphonic acids.—When sulphonated with 2 p.c. anhydro-acid at 70°, 100°, and 160°, 1-chloro-β-naphthylamine yields as chief product respectively the 5-, 6-, and 7-sulphonic acids (Armstrong and Wynne, Chem. Soc. Proc. 1889, 5, 36, 48). These acids when diazotised and heated in solution with excess of sodium carbonate at 50°–60°, are converted into the *diazo-oxides* of the corresponding 2-amino-α-naphtholsulphonic acids (Badische, D. R.-P. 145906, 148882; Eng. P. 6615 of 1902).

Nitro-β-naphthylamines.

(i.) 1-**Nitro-β-naphthylamine** is obtained when nitric acid of sp.gr. 1·4 (7 pts.) is added to acetyl-β-naphthylamine (9 pts.) suspended in acetic acid (12 pts.) in the cold, the crude product extracted by three times its weight of benzene (the residue consisting of acetyl-8-nitro-β-naphthylamine) and the crystalline separation from the filtrate de-acetylated by heating it with alcoholic caustic potash (Heilpern and Spielfogel, *cf.* J. Soc. Chem. Ind. 1898, 17, 836). It forms orange-yellow needles, m.p. 126°–127°, and dissolves readily in alcohol, but only moderately in hot water (Jacobson, Ber. 1881, 14, 1792; Liebermann and Jacobson, Annalen, 1882, 211, 64). The *acetyl* derivative, m.p. 123·5°, is converted into 1-*nitro-β-naphthol* when boiled with aqueous caustic soda (Jacobson, *ibid.* 806).

(ii.) 5-**Nitro-β-naphthylamine** is formed as chief product, together with the 8 isomeride, when β-naphthylamine nitrate (1 pt.) is stirred into monohydrate (4 pts.) at 0°, 20 p.c. anhydro-acid (2 pts.) being added gradually during the operation, and separates in the cold as sulphate when the nitration product is diluted with water (50 pts.), the more soluble sulphate of the 8-isomeride being retained in the mother liquor (Hirsch, D. R.-P. 57491; Eng. P. 9768 of 1890; Friedländer and Szymanski, Ber. 1892, 25, 2076). It forms red needles, m.p. 143·5°; its *acetyl* derivative yellow needles, m.p. 185·5°.

Reactions.—From its *diazo-* compound 5-*nitro-β-naphthol* has been obtained. By reduction with iron and acetic acid it yields 1 : 6-*diaminonaphthalene* (Friedlander and Szymanski, *l.c.*); but when boiled with sodium sulphite or bisulphite solution it is converted into a 1 : 6-*diaminonaphthalenesulphonic acid* (Read, Holliday & Sons, Eng. P. 26020 of 1896).

(iii.) 8-**Nitro-β-naphthylamine** (*v.* 5-nitro-β-naphthylamine) forms red needles, m.p. 103·5°, and its *acetyl* derivative, yellow needles, m.p. 195·5°. From its *diazo-* compound 8-*nitro-β-naphthol* can be obtained, and it gives 1 : 7-*diaminonaphthalene* on reduction (Friedlander and Szymanski, Ber. 1892, 25, 2081).

(iv.) 6-**Nitro-β-naphthylamine-8-sulphonic acid**, obtained by nitrating β-naphthylamine-8-sulphonic acid dissolved in sulphuric acid (Immerheiser, D. R.-P. 57023), gives a *barium* salt $BaA_2+4\frac{1}{2}H_2O$, and *ammonium* salt NH_4A, in red crystals (Jacchia, Annalen, 1902, 323, 119), and yields 2 : 6-*diaminonaphthalene* on reduction with sodium amalgam (Friedlander and Lucht, Ber. 1893, 26, 3033).

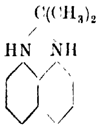
The 4 : 8-disulphonic acid is obtained by nitrating acetyl-β-naphthylamine-4 : 8-disulphonic acid in sulphuric acid solution and hydrolysing the product (Höchst, D. P. Anm. F. 31417).

V. Diamino- Derivatives.

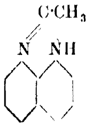
Introductory.—The existence of ten diaminonaphthalenes is to be expected on theoretical grounds, and ten have been identified. The methods employed in their production involve usually either replacement of OH by NH_2 in aminonaphthols or dihydroxynaphthalenes, or reduction of dinitronaphthalenes or nitronaphthylamines or of azo- dyes.

For the preparation of the 1 : 2- or 1 : 4-diaminonaphthalene, reduction of the *o-* or *p-* azo dyes of the naphthalene series by stannous chloride can be employed: and for that of the 1 : 3 derivative use is made of the naphthylamine- or naphthol-3-sulphonic acids, as these exchange the SO_3H group in the *meta-* position for an NH_2 radicle when heated with ammonia. These homonucleal compounds respectively resemble in properties, the *ortho-*, *para-* and *meta-* diamines of the benzene series.

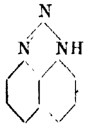
Of the heteronucleal compounds, the 1 : 5- and 1 : 8-diamines are the most important. The 1 : 5- derivative has been used for the production of disazo- dyes, but the interest attaching to the 1 : 8- derivative is due less to its property of coupling with diazotised bases than to the readiness with which—like the 1 : 2- and 2 : 3-diamines—it forms a third six-membered ring. Some of these *peri-* condensation products are coloured, others colourless, and, according to Sachs, colour or its absence is associated with the presence or absence of an unsaturated linking in the new ring (Annalen, 1909, 365, 53):



Colourless.



Green.



Red.

The diaminonaphthalenes crystallise well, but, as a rule, are less stable, and therefore less suitable for the production of dyestuffs,[1] than the respective diaminonaphthalenesulphonic acids. With nitrous acid, the 1 : 2-, 2 : 3-, and 1 : 8-diamines furnish azimino- compounds, but the 1 : 4- diamine is oxidised to [α-]naphthaquinone; the heteronucleal diamines, with the exception of the 1 : 8- isomeride, give tetrazo- derivatives of which that from the 1 : 5- diamine furnishes substantive disazo- dyes for cotton (Badische, D. R.-P. 39954).

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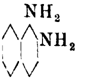
[1] 1-Arylsulphonyl derivatives of 1 : 4-diaminonaphthalene have a high degree of stability and can be used in the production of *ortho*-azo-dyes (Morgan and Grist, Chem. Soc. Trans. 1921, 119, 603; Morgan and Imperial Trust, Brit. P. 160853).

DIAMINONAPHTHALENES.



(i.) 1 : 2-**Diaminonaphthalene** is obtained by reducing azo- compounds derived from *β*-naphthylamine by coupling with diazotised bases (Griess, Ber. 1882, 15, 2193; Lawson, Ber. 1885, 18, 800, 2423; Sachs, *ibid.* 3128; Witt, Ber. 1886, 19, 2795; 1888, 21, 3482); *or* [β-]naphthaquinonedioxime (Koreff, Ber. 1886, 19, 179); *or* 2-nitro-*α*-naphthylamine (Lellmann and Remy, *ibid.* 803); *or* 1-nitro-*β*-naphthylamine (Lawson, *l.c.*; Lellmann and Remy, *l c.*) with stannous chloride in hydrochloric acid solution. It can also be obtained from 1 : 2-diaminonaphthalene-4-sulphonic acid (Friedlander and Kielbasinski, Ber. 1896, 29, 1978) or 3- or 5-sulphonic acid (Gattermann and Schulze, Ber 1897, 30, 53, 55) by interaction with sodium amalgam.

Preparation—On the laboratory scale, 10 grams of benzeneazo-*β*-naphthylamine, dissolved in 300 grams of boiling acetic acid (1 : 5), are reduced by adding zinc-dust in small quantities until the colour of the solution changes to bright yellow. The sulphate, obtained by filtering the boiling solution into dilute sulphuric acid, is then boiled with sodium carbonate solution until dissolved (Bamberger and Schieffelin, Ber. 1889, 22, 1376).

Identification.—It separates from hot water in silvery rhombic scales, m.p. 95°–96°, and is oxidised rapidly, becoming brown on exposure to the air. The *hydrochloride* $B{\cdot}2HCl$ forms short prisms easily soluble in water, and with ferric chloride gives an olive-green colouration, changing to brown and yellow; the *sulphate* $B_2{\cdot}H_2SO_4$, scales; the *diacetyl* compound, needles, m p. 234° (Lawson, *l c*). With benzil, [*β*-]naphthaquinone, phenanthraquinone (Lawson, *l c.*; Witt, *l.c.*), or glyoxal (Hinsberg, Ber. 1890, 23, 1394), it yields *quinoxalines*, and with nitrous acid a mixture of the two *azimino-* compounds (Morgan and Godden, Chem. Soc. Trans. 1910, 97, 1718).

The 1-*acetyl* derivative has been obtained, not by acetylation but mixed with the 1 : 4-compound (*q.v.*), by nitration of acetyl-*α*-naphthylamine and reduction of the product (Dahl, D. P. Anm. D. 6503).

2-Phenylamino-*α*-naphthylamine, broad needles or scales, m.p. 138°–140°, forming very sparingly soluble salts (Witt, Ber. 1887, 20, 573, 1184; Zincke and Lawson, *ibid.* 1170); and the 2-*p*-tolyl derivative, needles, m.p. 146°–147° (Fischer, Ber. 1892, 25, 2846), have been obtained by reduction of azo- derivatives of phenyl- and *p*-tolyl-*β*-naphthylamine.

(ii.) 1 : 3-**Diaminonaphthalene** is formed when 1 : 3-dinitronaphthalene is reduced with tin and hydrochloric acid (Urban, Ber. 1887, 20, 973). It is also produced when sodium *α*-naphthylamine- or *α*-naphthol-3-sulphonate is heated with ammonium chloride and 22 p c. ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061; Eng. P. 9103 of 1895); *or* when 1-amino-3-naphthol (Friedlander, Ber. 1895, 28, 1953), or 1 : 3-dihydroxynaphthalene (Friedlander and Rüdt, Ber. 1896, 29, 1612), is heated with concentrated aqueous ammonia under pressure at 150°.

Identification.—It crystallises from water in scales, m.p. 96°; its *hydrochloride* $B{\cdot}2HCl$ and *sulphate* in easily soluble needles, which in solution give a dark brown colouration with ferric chloride; the *diacetyl* compound in sparingly soluble needles, m.p. 263° (Friedländer, *l.c.*). With diazotised bases it gives chrysoidines, and with nitrous acid a deep yellow colouration (Urban, *l.c.*).

Diphenyl-1 : 3-diaminonaphthalene is obtained when *α*-naphthylamine-3-sulphonic acid (Bayer, D. R -P. 75296; Eng. P. 8898 of 1893), phenyl-*α*-naphthylamine-3-sulphonic acid (Bayer, D. R.-P. 78854; Eng. P. 19623 of 1893), or *α*-naphthol-3-sulphonic acid (Bayer, D. R.-P. 77866; Eng. P. 16780 of 1893) is heated with aniline and aniline hydrochloride at 150°–170°. It is insoluble in, and its *hydrochloride* is decomposed by water. The corresponding ditolyl, dixylyl, and phenyltolyl derivatives have also been prepared.

(iii.) 1 : 4-**Diaminonaphthalene** is formed by reducing azo- derivatives of *α*-naphthylamine with tin or stannous chloride and hydrochloric acid (Perkin, Chem Soc. Journ. 1865, 18, 173; Griess, Ber. 1882, 15, 2192. Friedlander, Ber. 1889, 22, 590) or with sodium hypo(hydro)sulphite (Grandmougin, Ber. 1906, 39, 3561); *or* by reducing 4-nitro-*α*-naphthylamine with tin and hydrochloric acid (Liebermann and Dittler, Annalen, 1876, 183, 238) It is also formed by hydrolysing 1 : 4-diaminonaphthalene-6-sulphonic acid (Cassella, D. R -P. 74177; Eng. P. 15444 of 1893).

Preparation.—On the laboratory scale, benzeneazo-*α*-naphthylamine is boiled with zinc-dust and water, the colourless solution filtered into dilute sulphuric acid, and the crystalline sulphate warmed with aqueous sodium carbonate for about 5 minutes (Bamberger and Schieffelin, Ber. 1889, 22, 1381).

Identification—It crystallises from water in needles or small prisms, m p. 120°, which when moist rapidly become coloured green and decompose. The *hydrochloride* $B{\cdot}2HCl$ forms readily soluble scales, and in neutral solution with ferric chloride gives a green colouration, changing to a brown precipitate of impure [*α*-]naphthaquinone (Griess, *l c.*); the *sulphate* $B{\cdot}H_2SO_4$, sparingly soluble needles; the *diacetyl* derivative, needles, m.p. 305° (Kleemann, Ber. 1886, 19, 334; Bamberger and Schieffelin, *l.c.*).

Reactions.—By nitrous acid (Grandmougin and Michel, Ber. 1892, 25, 977) or by dilute chromic acid solution, or ferric chloride, it is oxidised to [*α*-]*naphthaquinone.* Reduction in boiling amyl alcohol solution with sodium converts it into ar.-*tetrahydro*-1 : 4-*diaminonaphthalene*.

Monoacetyl-1 : 4-diaminonaphthalene is obtained, mixed with the 1 : 2- derivative, when acetyl-*α*-naphthylamine is stirred with 4 times its weight of 40 p.c. nitric acid at 0° during about 18 hours and the product reduced by iron. To separate the isomerides, the mixture (1 mol.) is either heated with dilute hydrochloric acid (1 mol.) at 80° when the hydrochloride of the 1 : 4- derivative passes completely into solution and can afterwards be salted out, or boiled with dilute sulphuric acid (½ mol.) when the sulphate being only sparingly soluble in the cold can be freed from the 1 : 2- derivative which remains in solution (Dahl, D. P. Anm. D. 6503). Unlike the diamine, which is not diazotisable, this compound can be used in the production of *disazo-* dyes, as the free amino-group can be diazotised and coupled before the acetylamino- group is de-acetylated.

unsymm.-Dimethyl-1 : 4-diaminonaphthalene, an oil (Friedlander and Welmans, Ber. 1888, 21, 3124); and the ethyl-, m.p. 152° (Kock, Annalen, 1888, 243, 312; Bamberger and Goldschmidt, Ber. 1891, 24, 2471); phenyl-, m.p. 148° (Wacker, Annalen, 1888, 243, 302; Fischer, Annalen, 1895, 286, 183); and α-naphthyl-diamino- derivatives (Wacker, *l c.*) have been described. The toluene-*p*-sulphonyl derivative forms tablets, m.p. 185°–186° (Morgan and Grist, Chem. Soc. Trans. 1921, 119, 605).

(iv.) 1 : 5-**Diaminonaphthalene** ([α-]*diaminonaphthalene*, *semi-naphthalidam*) is obtained from 1 : 5-dinitronaphthalene by reduction with ammonium sulphide (Zinin, Annalen, 1844, 52, 361), with tin and hydrochloric acid (Hollemann, Zeitsch. Chem. 1865, [ii.] 1, 556; Ladenburg, Ber. 1878, 11, 1651; Erdmann, Annalen, 1888, 247, 360), with stannous chloride and alcoholic hydrochloric acid (Meyer and Muller, Ber. 1897, 30, 773), or with phosphorus iodide and water (Aguiar, Ber. 1870, 3, 32; 1874, 7, 306). It is also formed when 1 : 5-dihydroxynaphthalene is heated either with ammonia under pressure at 250°–300° (Ewer and Pick, D. R.-P. 45549), or with ammonium bisulphite solution and ammonia at 125° (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900); *or* when 1 : 5-diaminonaphthalene-2-sulphonic acid is heated with dilute mineral acid (Friedlander and Kielbasinski, Ber. 1896, 29, 1983); *or* when α-naphthylamine is heated with naphthalene and sodamide at 230° (Sachs, Ber. 1906, 39, 3021).

Identification.—It crystallises in needles, m p. 189·5°, sublimes without decomposition, and with ferric chloride gives an intense bluish-violet colouration. The *hydrochloride* $B\cdot 2HCl$, and the *sulphate* $B\cdot H_2SO_4$ form moderately soluble needles, the *diacetyl* compound, m p. 360°, unlike the diamine, causes serious irritation of the skin (Kunckell and Schneider, Chem. Zeit. 1912, 36, 1021, 1226; *cf.* Chem. Fab. R. Scheuble & Co. *ibid.* 1226). It is convertible into 1 : 5-*dichloronaphthalene* (Erdmann, *l c.*).

Reactions.—With nitrous acid it yields a *tetrazo-* compound, and, by coupling with diazotised bases, *azo-* or *disazo-* dyes. Reduced in boiling amyl alcohol solution with sodium, it gives a mixture of ac.- and ar.- *tetrahydro*-1 : 5-*diaminonaphthalene.* By the bisulphite reaction, 1-*amino-5-naphthol* is the product. On sulphonation, its sulphate yields 1 : 5-*diaminonaphthalene-2-sulphonic acid.*

(v.) 1 : 6-**Diaminonaphthalene,** prepared by heating 1 : 6-dihydroxynaphthalene with ammonia under pressure at 150°–300° (Ewer and Pick, D. R.-P. 45788), *or* β-naphthylamine with sodamide and naphthalene at 230° (Sachs, Ber. 1906, 39, 3022), can be obtained pure by reducing either 5-nitro-β-naphthylamine with iron and acetic acid (Friedlander and Szymanski, Ber. 1892, 25, 2080; *cf.* Hirsch, D. R.-P. 57491; Dawson and Hirsch, Eng. P. 9768 of 1890), *or* 1 : 6-dinitronaphthalene with tin and hydrochloric acid (Kehrmann and Matis, Ber. 1898, 31, 2419).

Identification.—It crystallises from water in short needles, m.p. 77·5°, darkens on exposure to air, shows blue fluorescence in solution, and gives with ferric chloride a dark brownish-violet colouration. The *hydrochloride*, needles, is easily, but the *sulphate* $B\cdot H_2SO_4$, needles, only sparingly soluble in water; the *diacetyl* derivative, needles, m.p. 257°, dissolves sparingly in alcohol. The *tetrazo-* compound is convertible into 1 : 6-*dichloronaphthalene* (Friedlander and Szymanski, *l.c.*).

(vi.) 1 : 7-**Diaminonaphthalene** is prepared by reducing 8-nitro-β-naphthylamine in alcoholic solution with tin and hydrochloric acid (Friedländer and Szymanski, Ber. 1892, 25, 2082), *or* by heating 1 : 7-dihydroxy-β-naphthoic acid with ammonia under pressure at 200°–210° (Friedlander and Zinberg, Ber. 1896, 29, 40).

Identification.—It crystallises from water in needles, m p. 117·5°, gives with ferric chloride a violet colouration, and forms a *diacetyl* derivative, rhombohedra, m.p. 213°. The *tetrazo-* compound is convertible into 1 : 7-*dichloronaphthalene* (Friedlander and Szymanski, *l.c.*).

(vii.) 1 : 8-**Diaminonaphthalene** ([β-]*diaminonaphthalene*) can be obtained by reducing 1 : 8-dinitronaphthalene either with phosphorus iodide and water (Aguiar, Ber. 1874, 7, 306; Meyer and Muller, Ber. 1897, 30, 775), or with tin and hydrochloric acid (Ladenburg, Ber. 1878, 11, 1651; Erdmann, Annalen, 1888, 247, 363). It is also formed when 1 : 8-dihydroxynaphthalene is heated with ammonia under pressure at 250°–300° (Erdmann, *l.c.*).

Identification.—It crystallises from aqueous alcohol in needles, m.p. 67°, and in aqueous solution gives with ferric chloride a dark chestnut-brown colouration. The *hydrochloride* $B\cdot 2HCl$ forms very soluble scales, m.p. 280° (Ekstrand, Ber. 1887, 20, 1353); the *sulphate* $B\cdot H_2SO_4$, sparingly soluble needles; the *dibenzoyl* derivative, needles, m.p. 311°–312° (Sachs, Ber. 1906, 39, 3027); and the *oxalate*, either needles, m.p. 271° (Meyer and Müller, *l.c.*), or $BA+2H_2O$, decomp. 270°; B_2A, m.p. 205° (Sachs, Annalen, 1909, 365, 101).

Reactions.—Many condensation products can be obtained from this diamine. For example, with acetic anhydride it forms a green *anhydro-*compound, m.p. 210° (Sachs, Ber. 1906, 39, 3027); with ethyl oxalate, a red crystalline *perimidine-* derivative (Aguiar, *l.c.*; Meyer and Muller, *l.c.*; Sachs, Annalen, 1909, 365, 69, 96); with phthalic anhydride a yellow *perimidylbenzoic acid* or red *phthaloperinone*, needles, m.p. 227°–228° (Sachs, *ibid.* 117; Bayer, D. R.-P. 202354; Eng. P. 7575 of 1908); with acetone a colourless *dimethyldihydroperimidine* (*cf.* Sachs, *ibid.* 151; Badische, D. R.-P. 122475); with phosgene or alkyl carbonates, colourless *perimidones* (Sachs, *ibid.* 135).

With nitrous acid, it yields a red *azimino-* derivative, and *azo*-dyes by coupling it with diazotised bases. Its acid sulphate, when baked in a vacuum, is converted into 1 : 8-*diaminonaphthalene-4-sulphonic acid.* Boiled with sodium bisulphite solution and afterwards with alkali, it gives 1-*amino-8-naphthol*; but when heated with 17 p.c. hydrochloric acid at 180° the product is 1 : 8-*dihydroxynaphthalene.*

(viii.) 2 : 3-**Diaminonaphthalene** is obtained by heating 2 : 3-dihydroxynaphthalene either with 30 p c. ammonia solution under pressure at 250° (Höchst, D. R.-P. 73076; Friedländer and Zahrzewski, Ber. 1894, 27, 764), or with 30 p.c. ammonium sulphite solution and 20 p.c. ammonia at 80°, the product afterwards being acidified (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900).

Identification.—It crystallises from water in scales, m.p. 191°, and gives no colouration with ferric chloride. The *hydrochloride* is easily, but the *sulphate* only sparingly, soluble. The *diacetyl* derivative forms needles, m.p. 247°, convertible by prolonged boiling with acetic acid into an *anhydride*, m.p. 168°.

Reactions.—Its behaviour is that of an *o*-diamine. With nitrous acid it yields an *azimino*-derivative, yellow needles, m.p. 187°, and with diazotised bases (1 mol.) it couples giving red *azo*-dyes (Friedlander and Zahrzewski, *l.c.*).

The diphenyl derivative obtained by heating 2 : 3-dihydroxynaphthalene and aniline with 1 p.c. of iodine at 200°, forms needles, m.p. 143° (Knoevenagel, J. pr. Chem. 1914, [ii.] 89, 37).

(ix.) 2 : 6-**Diaminonaphthalene** is obtained when 2 : 6-dihydroxynaphthalene is heated with ammonia under pressure at 150°–300° (Ewer and Pick, D. R.-P. 45788); *or* with ammonia and ammonium chloride at 200°–250° (Lange, Chem. Zeit. 1888, 12, 856); *or* with ammonia-calcium chloride at 270° (Jacchia, Annalen, 1902, 323, 132). It is also formed by reduction of 2 : 6-diaminonaphthalene-4-sulphonic acid with sodium amalgam (Friedländer and Lucht, Ber. 1893, 26, 3033).

Identification.—It crystallises in scales, m.p. 216°, darkens on exposure to the air, and with ferric chloride gives a green colouration, which changes to blue when the solution is warmed. The *sulphate* is sparingly soluble; the *diacetyl* derivative forms needles.

The diphenyl derivative, obtained by heating 2 : 6-dihydroxynaphthalene with aniline and aniline hydrochloride at 170°, melts at 210° (Leonhardt, D. R.-P. 54087; Eng. P. 3098 of 1890).

(x.) 2 : 7-**Diaminonaphthalene** is obtained when 2 : 7-dihydroxynaphthalene is heated with ammonia under pressure at 150°–300° (Ewer and Pick, D. R.-P. 45788); *or* with ammonia and ammonium chloride at 200°–250° (Lange, Chem. Zeit. 1888, 12, 856); *or* with ammonia-calcium chloride at 260°–270° (Bamberger and Schieffelin, Ber. 1889, 22, 1384); *or* boiled with ammonium sulphite solution and ammonia (Franzen and Deibel, J. pr. Chem. 1908, [ii.] 78, 155). It is also formed from 2-amino-7-naphthol by the bisulphite reaction (Bucherer, J. pr. Chem. 1904, [ii.] 69, 80; *v.* p. 416).

Identification.—It crystallises from water in scales, m.p. 161°, and gives no colouration with ferric chloride. Its salts are easily soluble. The *diacetyl* derivative forms needles, m.p. 254°.

Reactions.—Diazotised in acetic acid solution, it yields only a *diazo-* compound (Kaufler and Karrer, Ber. 1907, 40, 3263), but in sulphuric acid a *tetrazo-* derivative convertible into 2 : 7-*dichloronaphthalene* (Morgan and Micklethwait, Chem. Soc. Trans. 1910, 97, 2558). By the bisulphite reaction it furnishes 2-*amino*-7-*naphthol*.

Diphenyl-2 : 7-diaminonaphthalene, obtained when 2 : 7-dihydroxynaphthalene is heated with aniline and aniline hydrochloride at 140°–180° (Durand and Huguenin, D. R.-P. 40886; Annaheim, Eng. P. 14283 of 1886; Ber. 1887, 20, 1372), forms scales, m.p. 163°–164°; its *diacetyl* derivative, small crystals, m.p. 197·5° (Clausius, Ber. 1890, 23, 528); and its *tetramethyl*-p-*diamino-* compound, obtained by interaction of *p*-aminodimethylaniline and 2 : 7-dihydroxynaphthalene at 200°–220°, ill-defined crystals, m.p. 180° (Aktienges., D. R.-P. 75044).

The *o*-tolyl, m.p. 106°; *p*-tolyl, m.p. 236°–237°; and *m*-xylyl, m.p. 130°, derivatives have also been prepared (Durand and Huguenin, *l.c.*).

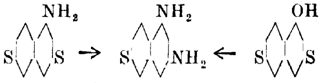
DIAMINONAPHTHALENESULPHONIC ACIDS.

The methods by which sulphonic acids of the heteronucleal diaminonaphthalenes can be obtained do not lend themselves to generalisation; those for the production of homonucleal diaminonaphthalenesulphonic acids can be summarised—

(i.) For 1 : 2- or 1 : 4-diaminonaphthalenesulphonic acids: Reduction of azo-dyes formed by coupling diazotised bases with the appropriate *β*- or *α*-naphthylaminesulphonic acids (*cf.* Witt, Ber. 1888, 21, 3485; Reverdin and de la Harpe, Ber. 1892, 25, 1403; 1893, 26, 1281).

When, as may be the case with azo-dyes obtained by coupling with *α*-naphthylamine-3- or 5-sulphonic acid, a mixture of the 1 : 2- and 1 : 4-diaminonaphthalenesulphonic acids is obtained, the ready solubility of the 1 : 2- derivative in sodium sulphite solution in the cold affords a convenient means for achieving their separation (Gattermann and Liebermann, Annalen, 1912, 393, 206).

(ii.) For 1 : 3-diaminonaphthalenesulphonic acids: Interaction of *α*-naphthylamine- or *α*-naphthol-3-sulphonic acids with ammonia at high temperatures (Kalle, D. R.-P. 89061; Eng. P. 9103 of 1895)



Diaminonaphthalenesulphonic acids are used technically for the production of azo-dyes and azine dyes.

For azo- dyes.—Diaminonaphthalenesulphonic acids yield azo-dyes, by coupling with diazotised bases, if derived from the 1 : 3-, 1 : 5-, and 2 : 7-diamines. Like the base itself, 1 : 5-diaminonaphthalene-3 : 7-disulphonic acid furnishes a tetrazo- compound which, when coupled, gives direct cotton dyes (Cassella, D. R.-P. 62075; Eng. P. 15346, 15347 of 1890).

1 : 4-Diaminonaphthalenesulphonic acids do not couple with diazotised bases. By nitrous acid, they are usually oxidised, but azo-dyes can be made from them by employing the monoacetyl derivatives in which the one amino- group can be diazotised and coupled before the other is de-acetylated (*cf.* Cassella, D. R.-P. 78831; 79910; Eng. P. 15444 of 1893). The 2-sulphonic acid can be diazotised in acetic or oxalic acid solution, but only one amino- group is attacked until the product has been coupled with a naphthol, when the second becomes reactive, and by coupling furnishes substantive disazo-dyes for cotton (Levinstein, D. R.-P. 102160; Eng. P. 2946, 17064 of 1896).

1 : 8-Diaminonaphthalenesulphonic acids form azimino- derivatives with nitrous acid. They couple with diazotised bases forming *azo*-dyes, but a marked increase in fastness and purity of shade is obtained if instead of the diamino- acids their acetone condensation products (dimethyldihydroperimidines) are used

(Badische, D. R.-P. 121228, 122475; Eng. P. 12819 of 1900), or if the azo-dyes, formed by coupling 1 : 8-diaminonaphthalenesulphonic acids with diazotised bases, are converted into azimino- derivatives (Cassella, D. R.-P. 77425; *Eng. P. 24714 of 1893; D. R.-P. 139908; Eng. P. 26147 of 1901; Bayer, D. R.-P. 222928; cf.* Höchst, D. R.-P. 143387; Eng. P. 953 of 1903).

For azines.—The sulphonic acids employed in the production of azine dyes have been those derived from the diaryl-1 : 3-diaminonaphthalenes (Bayer, D. R.-P. 78497, 77189, 80778, 86223, 86224; Eng. P. 8898, 11892 of 1893), and from the diaryl-2 : 6- and diaryl-2 : 7-diaminonaphthalenes (Leonhardt, D. R.-P. 54087; Eng. P. 3098 of 1890).

The sources and general characters of diaminonaphthalenesulphonic acids are summarised in the following tables, references to fluorescence, usually green in colour, or non-fluorescence of solutions of the alkali salts being omitted, for want of room :—

Diaminonaphthalenemonosulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S **1 : 2 : 3**	Reduction of azo-derivatives of α-naphthylamine-3-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 54).	*Acid*, HA, broad needles. Gives intense emerald-green colouration with ferric chloride.
1 : 2 : 4	Reduction of azo-derivatives of α-naphthylamine-4-sulphonic acid (Witt, Ber. 1886, 19, 1720); *or* of congo-red (Friedländer and Kielbasinski, Ber. 1896, 29, 1978).	*Acid*, sp. soluble needles Is decomposed by nitrous acid and does not couple. *Acetyl* derivative converted into ethenyl compound by mineral acids or heat (Lange, D. R.-P. 57942).
1 : 2 : 5	Reduction of azo-derivatives of α-naphthylamine-5-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 53); *or* of β-naphthylamine-5-sulphonic acid (Witt, Ber. 1888, 21, 3486).	*Acid*, HA, sparingly soluble leaflets. Is decomposed by nitrous acid and does not couple with diazotised bases.
1 : 2 : 6	Reduction of azo-derivatives of β-naphthylamine-6-sulphonic acid (Witt, Ber. 1888, 21, 3484).	*Acid*, sparingly soluble needles; *sodium* salt, scales. Is decomposed by nitrous acid and does not couple with diazotised bases.
1 : 2 : 7	Reduction of azo-derivatives of β-naphthylamine-7-sulphonic acid (Witt, Ber. 1888, 21, 3485).	*Acid*, grey powder. Is decomposed by nitrous acid and does not couple with diazotised bases.
1 : 3 : 5	α-Naphthol-3 : 5-disulphonic acid heated with ammonia under pressure at 175° (Kalle, D. R.-P. 94075).	*Acid*, readily sol. Couples with diazotised bases. For *diaryl* derivatives, *cf.* Bayer, D. R.-P. 77866, 78854; Eng. P. 16780, 19623 of 1893.
1 : 3 : 6	α-Naphthylamine- or α-naphthol-3 : 6-disulphonic acid heated with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061, 94075; Eng. P. 9103 of 1895; Friedländer and Taussig, Ber. 1897, 30, 1462).	*Acid*, sparingly; *sodium* salt, readily soluble. Forms yellow *diazo*-compound. Couples with diazotised bases. For *diaryl* derivatives, *cf.* Bayer, D. R.-P. 76414, 77866, 78854; Eng. P. 8898, 16780, 19623 of 1893.
1 : 3 : 7	α-Naphthylamine- or α-naphthol-3 : 7-disulphonic acid heated with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061; Eng. P. 9103 of 1895).	*Acid*, very sparingly soluble needles. Gives reddish-brown colouration with ferric chloride. For *diaryl* derivatives, *cf.* Bayer, *l.c.*
1 : 3 : 8	α-Naphthylamine- or α-naphthol-3 : 8-disulphonic acid heated with ammonia under pressure at 160°–180° (Kalle, D. R.-P. 89061; Eng. P. 9103 of 1895).	*Acid*, very sparingly soluble. Gives reddish-brown colouration with ferric chloride. For *diaryl* derivatives, *cf.* Bayer, *l.c.*
1 : 4 : 2	(1) Reduction of azo-derivatives of α-naphthylamine-2-sulphonic acid (Levinstein, D. P. Anm. C. 5930; Eng. P. 2946 of 1896; Oesterreich, *cf.* J. Soc. Chem Ind. 1898, 17, 836). (2) Action of sodium bisulphite on [α-] naphthaquinonechlorimide (Friedländer and Reinhardt, Ber. 1894, 27, 239).	*Acid*, very sparingly soluble. Gives dark green colouration with ferric chloride. In acetic acid solution forms *diazo*-compound with nitrous acid (1 mol.), convertible into *α-naphthylamine-3-sulphonic acid* and by coupling into *azo*-dyes in which the second amino-group can be diazotised and coupled to furnish *disazo*-dyes (Levinstein, *l.c.*; D. R.-P. 102160).
1 : 4 : 5	Reduction of 4-nitro-α-naphthylamine-5-sulphonic acid (Bayer, D. R.-P. 133951; Levinstein, Eng. P. 13178 of 1899).	*Acid*, greyish needles, rapidly oxidised in alkaline solution.
1 : 4 : 6	(1) Sulphonation of acetyl-1 : 4-diaminonaphthalene with 20 p.c. anhydro-acid at 25°–50° and subsequent de-acetylation (Dahl, D. R.-P. 66354; Ammelburg, J. pr. Chem. 1893, [ii.] 48, 286) (2) Reduction of azo-derivatives of α-naphthylamine-6- or 7-sulphonic acid (Levinstein, Eng. P. 12119 of 1898; Cassella, D. R.-P. 116922). (3) As the mixed 1- and 4-acetyl derivatives by nitrating a mixture of acetylated α-naphthylamine-6- and 7-sulphonic acids and after salting out reducing the product (Cassella, D. R.-P. 74177; Eng. P. 15444 of 1893).	*Acid*, very sparingly soluble. With nitrous acid or ferric chloride forms [α-]*naphthaquinone* (Dahl, *l.c.*). *Formyl* derivative (Gaess, D. R.-P. 138030, 138031; Eng. P. 3152; 8195 of 1902). *Acetyl* derivative (Dahl, *l.c.*; *cf.* Bayer, D. R.-P. 109609); *acid*, HA, needles, and *lead* salt, $PbA_2+1\frac{1}{2}H_2O$, very sparingly, but *zinc*, $ZnA_2+3\frac{1}{2}H_2O$, needles, *barium*, BaA_2+7H_2O, flat prisms, and *potassium* salt, KA, needles, easily soluble (Ammelburg, *l.c.*). Gives brilliant blue colouration with ferric chloride and is diazotised by nitrous acid.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S		
1 : 5 : 2	(1) Reduction of 5-nitro-α-naphthylamine-2-sulphonic acid (Cassella, D. R.-P. 70890; Friedländer and Kielbasinski, Ber. 1896, 29, 1983). (2) Sulphonation of 1 . 5-diaminonaphthalene sulphate with 5 p.c. anhydro-acid at 100° (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 213).	*Acid*, sparingly soluble small needles; *sodium* salt readily; *barium* salt, BaA_2, sparingly soluble. Forms an easily soluble yellow *tetrazo*-compound. Couples with 1 mol. or 2 mols. of a diazotised base.
1 : 5 : 3	Nitration and reduction of α-nitronaphthalene-7-sulphonic acid (Cassella, D. R.-P. 85058), *or*, mixed with 1 : 8 : 3-acid, of naphthalene-β-sulphonic acid (Cassella, D. R.-P. 67017; Eng. P. 6972 of 1891).	*Acid*, sparingly, salts readily soluble: ***hydrochloride***, prisms. Forms a *tetrazo*-compound.
1 : 5 : 4	(1) Reduction and de-acetylation of 5-nitroacetyl-α-naphthylamine-4-sulphonic acid (Nietzki and Zubelen, Ber. 1889, 22, 451; Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 255). (2) From 1 . 5-dihydroxynaphthalene-4-sulphonic acid heated with ammonium bisulphite solution and ammonia (Bucherer and Uhlmann, *l.c.*).	*Acid*, very sparingly soluble. Forms a *tetrazo*-compound. Couples with diazotised bases.
1 : 6 : 4	1-Amino-6-naphthol-4-sulphonic acid heated with ammonia under pressure at 170°–180° (Dahl, D. R.-P. 65834, 71157; Eng. P. 4110 of 1892; Friedlander and Kielbasinski, Ber. 1896, 29, 1979).	*Acid*, very sparingly soluble needles; *barium* and *sodium*, $NaA + 1\frac{1}{2}H_2O$, salts flat prisms moderately soluble. Forms a *tetrazo*-compound which decomposes at 0° into a *diazonaphtholsulphonic acid*. Couples with diazotised bases.
1 : 8 : 3	Nitration and reduction of α-nitronaphthalene-6-sulphonic acid (Cassella, D. R.-P. 85058), *or*, mixed with 1 . 5 : 3-acid, of naphthalene-β-sulphonic acid (Cassella, D. R.-P. 67017; Eng. P. 6972 of 1891).	*Acid*, sparingly soluble needles; *alkali* salts readily soluble; *hydrochloride* needles. Forms an *azimino*-derivative. Couples with 1 mol. or 2 mols. of diazotised bases.
1 : 8 : 4	(1) Reduction of 1 . 8-dinitronaphthalene-4-sulphonic acid (Cassella, D. R.-P. 70019; Eng. P. 4613 of 1893). (2) Acid sulphate of 1 : 8-diaminonaphthalene 'baked' above 100° in a vacuum (Bayer, D. R.-P. 216075, Eng. P. 6831 of 1909).	*Acid*, almost insoluble, *sodium* salt readily soluble; *hydrochloride* and *sulphate* crystallise well. Forms an *azimino*-derivative (*cf.* Cassella, D. R.-P. 77425; Eng. P. 24714 of 1893). Couples with 1 mol. or 2 mols. of diazotised bases.
2 : 3 : 6	2 : 3-Dihydroxynaphthalene-6-sulphonic acid or 2-amino-3-naphthol-6-sulphonic acid, heated with ammonia under pressure at 150°–220° (Aktienges., D. P. Anm. A. 3676, Eng. P. 8381 of 1894; Oesterreich, *cf.* J. Soc. Chem. Ind. 1898, 17, 836).	*Acid*, sparingly soluble; *sodium* salt leaflets, showing blue fluorescence in solution; *barium* salt, BaA_2. Gives brown colouration with ferric chloride. Forms an *azimino*-derivative. Couples with 1 mol. of diazotised bases (Oesterreich, *l.c.*) but with 2 mols. of diazotised *p*-nitraniline (Aktienges., D. R.-P. 84461).
2 : 6 : 4	Reduction of 6-nitro-β-naphthylamine-8-sulphonic acid (Friedlander and Lucht, Ber. 1893, 26, 3033).	*Acid*, sparingly soluble flat prisms. Gives emerald-green colouration with ferric chloride (Jacchia, Annalen, 1902, 323, 130).

Diaminonaphthalenedisulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S : S		
[illegible] : 2 : 3 : 6	Reduction of azo-derivatives of α-naphthylamine-3 : 6-disulphonic acid (Witt, Ber. 1888, 21, 3487).	*Acid*, sparingly soluble; *acid sodium* salt, NaHA, needles. Gives emerald-green colouration with ferric chloride. Decomposed by nitrous acid. Does not couple in acid solution (Cassella, D. R.-P. 72584).
1 : 2 : 3 : 8	Reduction of azo-derivatives of α-naphthylamine-3 . 8-disulphonic acid (Bernthsen, Ber. 1890, 23, 3094).	*Acid sodium* salt, $NaHA + 3H_2O$, needles. *Anhydride* (sultam), $C_{10}H_8O_5N_2S_2 + 2H_2O$, sparingly soluble long needles.
1 : 3 :(5): 7	α-Naphthol-3 : 5 : 7-trisulphonic acid heated with ammonia and ammonium chloride under pressure at 160°–180° (Kalle, D. R.-P. 90906, Eng. P. 9103 of 1895).	*Acid*, very sparingly soluble needles. Gives yellowish-red colouration with ferric chloride, and brown with nitrous acid. Couples with diazotised bases.
1 : 3 : 6 : 8	α-Naphthol- or α-naphthylamine-3 . 6 . 8-trisulphonic acid heated with ammonia and ammonium chloride at 160°–180° (Kalle, D. R.-P. 90905; Eng. P. 9103 of 1895).	*Acid*, sparingly soluble leaflets. Gives intense green colouration with ferric chloride and brown with nitrous acid. Couples with diazotised bases. For *diaryl*-derivatives, *cf.* Bayer, D. R.-P. 77866, 78854; Eng. P. 16780, 19623 of 1893.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : N : S : S 1 : 5 : 3 : 7	Reduction of 1 : 5-dinitronaphthalene-3 : 7-disulphonic acid (Cassella, D. R.-P. 61174; Eng. P. 15346 of 1890; *cf.* Oehler, D. P. Anm. O. 1430; Bayer, D. R.-P. 126198).	*Acid*, very sparingly soluble leaflets; *sodium* and *barium* salts sparingly soluble. Forms an insoluble *tetrazo*-compound (*cf.* Cassella, D. R.-P. 62075; Eng. P. 15346 of 1890). Couples with diazotised bases.
1 : 5 : 4 :(8)	1 : 5-Dinitronaphthalene heated with sodium bisulphite solution in a reflux apparatus or under pressure (Fischesser, D. R.-P. 79577; Eng. P. 13156 of 1894).	*Acid*, readily soluble; *acid barium* salt, $Ba(HA)_2 + 10H_2O$, moderately soluble. Gives a reddish-blue colouration with ferric chloride. Forms a *tetrazo*-compound, and couples.
1 : 6 : 3 : 8	Reduction of 1 : 6-dinitronaphthalene-3 : 8-disulphonic acid (Friedländer and Kielbasinski, Ber. 1896, 29, 1982; *cf.* 2574).	*Acid*, sp. sol.; *sodium* salt, Na_2A, easily soluble needles showing violet fluorescence in solution. Couples with diazotised bases.
1 : 6 : 4 : 8	Reduction of 1 : 6-dinitronaphthalene-4 : 8-disulphonic acid (Kalle, D. R.-P. 72665; Friedländer and Kielbasinski, Ber. 1896, 29, 1980; *cf.* 2574).	*Acid*, sparingly soluble. Gives cherry-red colouration with ferric chloride. Forms a sparingly soluble *tetrazo*-compound. Couples with diazotised bases.
1 : 8 :(2): 5	1 : 8-Diaminonaphthalene-4-sulphonic acid sulphonated with 8 p.c. anhydro-acid at 80° (Cassella, D. R.-P. 72584).	*Acid* and *sodium* salt readily soluble. Forms an *azimino*-derivative. Couples readily with 1 mol., less readily with 2 mols., of diazotised bases.
1 : 8 : 3 : 6	Reduction of 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid (Cassella, D. R.-P. 67062; Eng. P. 1742 of 1891; Bayer, D. R.-P. 69190; Eng. P. 11522 of 1892).	*Acid potassium* salt, $KHA + 3H_2O$, needles; *acid barium* salt, $Ba(HA)_2 + 6H_2O$, sparingly soluble needles. Gives reddish-brown colouration with ferric chloride. Forms an *azimino*-derivative (Cassella, D. R.-P. 69963). Couples with diazotised bases.
2 : 3 : 6 : 8	2-Amino-3-naphthol-6 : 8-disulphonic acid heated with 30 p.c. ammonia under pressure at 185°–190° (Aktienges., D. R.-P. 86448; Eng. P. 8645 of 1895).	*Acid*, sparingly soluble needles; *sodium* salt, readily soluble.
2 : 6 : ? : ?	2 : 6-Dihydroxynaphthalenedisulphonic acid heated with ammonia and ammonium chloride under pressure at 200° (Jacchia, Annalen, 1902, 323, 131).	*Acid*, $H_2A + 4\frac{1}{2}H_2O$ leaflets.
2 : 7 : 3 : 6	2 : 7-Dihydroxynaphthalene-3 : 6-disulphonic acid heated with ammonia under pressure at 200°–220° (Aktienges., D. P. Anm. A. 3686; Eng. P. 3844 of 1894).	*Acid*, sparingly, *sodium* salt, readily soluble. Gives faint brown colouration with ferric chloride. Forms a sparingly soluble *tetrazo*-compound. Couples with diazotised bases.

1 : 8-Diaminonaphthalene-2 : 4 : (7 or 6)-trisulphonic acid, obtained when 1 : 8-dinitronaphthalene is heated with sodium bisulphite solution (Fischesser & Co., D. R.-P. 79577; Eng. P. 13156 of 1894). The *acid sodium* salt $Na_2HA + 2H_2O$, is readily soluble, but the *acid barium* salt, $BaHA + 2H_2O$, only sparingly soluble. The colouration with ferric chloride is yellowish-brown. It forms an *azimino*-derivative, and couples with 1 mol. of a diazotised base.

TRIAMINONAPHTHALENES.

(i.) 1 : 2 : 6-Triaminonaphthalene, obtained by reduction of 1 : 6-dinitro-β-naphthylamine (*cf.* Kehrmann and Matis, Ber. 1898, 31, 2419), forms a *triacetyl* derivative, needles, m.p. 280°, and gives the reactions of an *o*-diamine (Loewe, Ber. 1890, 23, 2544).

(ii.) 1 : 3 : 6-Triaminonaphthalene, obtained by heating 1 . 6-dihydroxynaphthalene-3-sulphonic acid with ammonia and ammonium chloride under pressure at 160°–180°, is easily, but its *sulphate* only sparingly soluble. Its solution is coloured deep brown by nitrous acid (Kalle, D. R.-P. 89061; Eng. P. 9103 of 1895).

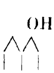
(iii.) 1 : 3 : 7-Triaminonaphthalene obtained by heating 1 : 7-dihydroxynaphthalene-3-sulphonic or 2-amino-6-naphthol-8-sulphonic acid with ammonia and ammonium chloride at 160°–180°, is easily soluble and in solution gives a deep brown colouration with nitrous acid, but bluish-violet with ferric chloride. The *sulphate* is only sparingly soluble (Kalle, D. R.-P. 90905; Eng. P. 9103 of 1895).

VI. HYDROXY- DERIVATIVES.

Introductory.—α - Naphthol, β- naphthol, several of the α- and β-naphtholsulphonic acids, and the greater number of the dihydroxynaphthalenes, are obtained on the large scale from the appropriate naphthalenesulphonic acids by fusion with caustic potash or soda. An alternative method, also of wide application, for the production of hydroxy-derivatives is that in which naphthylaminesulphonic acids are used, the exchange of the amino- group for hydroxyl being effected by the diazo- reaction, by the bisulphite method, or by water at a high temperature.

In general, the hydroxynaphthalenes resemble the hydroxybenzenes in chemical behaviour and properties, and the resemblance is complete when, by hydrogenation of the non-substituted ring, *ar.*- derivatives are formed from them (*cf.* Bamberger, Annalen, 1890, 257, 10). Nevertheless, in certain directions, differences exist between the two series, as may be illustrated by reference to the two naphthols. These compounds, and β-naphthol more readily than α-naphthol, are converted into naphthylamines when heated with ammonia under pressure (Badische, D. R.-P. 14612; Eng. P. 2516 of 1880), into alkyl ethers when heated with alcohol and hydrochloric acid at 150° (Liebermann and Hagen, Ber. 1882, 15, 1427), and into naphthyl ethers when boiled with dilute sulphuric acid (Graebe, Ber. 1880, 13, 1850), whereas phenol under similar conditions yields, at most, only traces of the corresponding products. Similar differences can be recognised when the dihydroxynaphthalenes are compared with the dihydroxybenzenes.

HYDROXYNAPHTHALENES.



(i.) α-**Naphthol** occurs in very small amount in coal tar fractions of high boiling-point (Schulze, Annalen, 1885, 227, 150). It was first obtained from α-naphthylamine by the diazo- reaction (Griess, Proc. Roy. Soc 1862, 12, 419), but on the large scale is prepared by fusing sodium naphthalene-α-sulphonate with caustic soda or potash (*cf.* Schaffer, Annalen, 1869, 152, 281; Willson and Meyer, Ber. 1914, 47, 3162). It is also formed by digesting α-chloronaphthalene with 10 p.c. caustic soda solution at 280°–300° (Meyer and Bergius, Ber. 1914, 47, 3159) or in better yield with caustic soda and methyl alcohol at 210° (Chem. Werke. Ichendorf, D. R.-P. 281175), or, free even from traces of β-naphthol, by heating α-naphthylamine salts with water under pressure.

Preparation.—The process adopted in the manufacture of α-naphthol from sodium naphthalene-α-sulphonate is practically identical with that described under β-naphthol (*q.v.*, *cf.* Levinstein, Eng. P. 2300 of 1883). Alternatively, α-naphthylamine hydrochloride or sulphate is heated with 5 times its weight of water under pressure at 200° for 1–4 hours, and the product distilled to remove small quantities of impurities of high boiling-point (Hochst, D. R.-P. 74879; Eng. P. 14301 of 1892); *or* α-naphthylamine is heated with sodium bisulphate, phosphoric acid, or zinc chloride and water at 210° (Höchst, D. R.-P 76595).

Properties.—α-Naphthol crystallises in lustrous monoclinic flat prisms (*cf.* Steinmetz, Z. Kryst. Min. 1916, 55, 375) m.p. 94°, b.p. 278°–280° (Schäffer, *l.c.*), sp.gr. 1·224 at 4° (Schroder, Ber. 1879, 12, 1613), and dissolves readily in alcohol, organic solvents, or in solutions of caustic alkalis, but only very sparingly in hot water. Its odour is phenolic and it volatilises readily with steam.

Reactions.—It couples with diazotised bases forming para-*azo*- dyes, but in alcoholic solution with benzenediazonium chloride, is said to give a mixture of the *ortho*- and *para*- compounds, of which the former is insoluble in 4 p.c. caustic soda solution (Charrier and Casale, Atti R. A. Sci. Torino, 1914, 49, 477). By nitrous acid it is converted into a mixture of 2-*nitroso*- and 4-*nitroso-α-naphthol* (*v. Naphthaquinoneoximes*), the former as chief product, or, in ethereal solution, into 2 : 4-*dinitro-α-naphthol*, which is also the product of nitration. Chlorination with sulphuryl chloride converts it into 4-*chloro*-, but with chlorine into 2 : 4-*dichloro-α-naphthol*. By sulphonation α-*naphthol-mono*-, *di*-, and *trisulphonic acids* are obtained.

Oxidation with nitric acid or with permanganate in acid solution furnishes *phthalic acid*, but with permanganate in alkaline solution *phthalonic acid* is obtained (Henriques, Ber. 1888, 21, 1608), and in caustic soda solution with cupric oxide at 250° a mixture of *benzoic* and *phthalic acids* (Bindsch., D. R.-P. 138790, 139956). On reduction with sodium in amyl alcohol solution, it yields ar.-*tetrahydro-α-naphthol* as the sole product. When heated under pressure with ammonia, acetamide or aniline, it is converted respectively into *α-naphthylamine*, or its *acetyl* or *phenyl* derivative. Its dry sodium compound,[1] when heated with carbon dioxide under pressure, yields 1-*hydroxy*-2-*naphthoic acid*

It is converted into *α-dinaphthylene oxide* $(C_{10}H_6)_2O$ when boiled for some time in the air, when distilled with litharge, or, mixed with naphthalene and other products, when heated in a tube at 350°–400° (Graebe, Knecht, and Unzeitig, Annalen, 1881, 209, 134; Merz and Weith, Ber. 1881, 14, 195).

Colour reactions—Bleaching-powder solution, added to an aqueous solution of α-naphthol, gives first a dark-violet colouration and then a flocculent precipitate of the same colour; but ferric chloride produces a milky opalescence, which changes to a violet flocculent precipitate of *αα′-dinaphthol* (Schaffer, *l.c.*; Dianin, Ber. 1873, 6, 1252; 1874, 7, 487). Like β-naphthol, it develops a Prussian-blue colouration with chloroform and caustic potash solution, but, unlike β-naphthol, it gives a deep violet turbid liquid when mixed in aqueous solution with sodium hypoiodite (Jorissen, Ann. Chim. anal. 1902, 7, 217), and an intense green colouration, changing to reddish-violet on addition of acetic acid, when shaken in small amount (0·01–0·02 g.) with 2–3 c.c. of titanyl sulphate solution[2] (Denigès, Ann Chim anal. 1916, 21, 216).

Tests.—Commercial α-naphthol should be colourless, have a melting-point very nearly that of the pure compound, and leave only a small residue on extraction with caustic alkali solution.

Estimation.—The *picrate*, m.p. 189°–190°, which is almost insoluble in water (Marchetti, Gazz. chim. ital. 1882, 12, 503), can be employed in the quantitative estimation of α-naphthol. The sample is heated with N/20 picric acid solution in a closed vessel, and the excess of picric acid afterwards determined by titration with N/10 baryta, lacmoid being the indicator (Küster, Ber. 1894, 27, 1104).

α-**Naphthyl methyl ether** (*α-methoxynaphthalene*), formed by heating sodium α-naphtholate with methyl chloride and methyl alcohol under pressure at 100° (Bayer, Eng. P. 1168 of 1879); *or* by passing methyl chloride through sodium α-naphtholate at 280° (Vincent, Bull. Soc. chim. 1883, [ii.] 40, 107); *or* by leading a solution of α-naphthol in methyl alcohol into naphthalene-β-sulphonic acid at 140°–145° (Krafft & Roos, D. R.-P. 76574; Eng. P. 6190 of 1894); *or* by heating α-naphthylamine with methyl alcohol and zinc chloride at 180°–200° (Hantzsch, Ber. 1880, 13, 1347), is conveniently prepared by heating α-naphthol (5 pts.) with absolute methyl alcohol (5 pts.) and sulphuric acid (2 pts.) at 140° in a reflux apparatus provided with a small mercury column (Gattermann, Annalen, 1888, 244, 72). It is an oil with an orange-like odour, b.p. 269°, sp.gr. 1·0974 at 15°, and is volatile with steam.

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[1] Crystalline sodium α- or β-naphtholate can be obtained by dissolving the naphthol (1 pt.) in boiling 7·5 p.c. caustic soda solution (4 pts.) to which, afterwards, common salt (1 pt.) is added (König, D. R.-P. 216596).

[2] Prepared by heating rutile with concentrated sulphuric acid during some hours near the boiling-point.

α-**Naphthyl ethyl ether**, formed by methods similar to those described for the methyl ether (*cf.* Schaffer, Annalen, 1869, 152, 286; Liebermann and Hagen, Ber. 1882, 15, 1427; Gattermann, *l.c.*), can be prepared by heating α-naphthol (72 g.) with 36 p.c. caustic potash (85 c.c.) and potassium ethyl sulphate (90 g.) for 6 hours under pressure at 150°, any unchanged α-naphthol being removed by coupling with diazotised sulphanilic acid (Witt and Schneider, Ber. 1901, 34, 3173). It is an oil of peculiar odour, m.p. 5·5°, b.p. 276°, and is volatile with steam.

Reactions.—Like other α-naphthyl ethers, it couples with diazotised bases containing *p*- or *op*- negative radicles, *e.g.* diazotised 2 : 4-dinitroaniline, forming *azo*- dyes (Meyer, Irschick and Schlösser, Ber. 1914, 47, 1750). On sulphonation it yields *ethoxy-α-naphthol-4-sulphonic acid*, from which by nitration 2 : 4-*dinitro-α-naphthol*, 4-*nitro α-naphthyl ethyl ether*, and 2-*nitro*-1-*ethoxynaphthalene*-4-*sulphonic acid* are formed (Witt and Schneider, *l.c.*).

α-**Naphthyl phenyl ether**, m.p. 55°–56°, is obtained by heating a solution of sodium α-naphtholate in α-naphthol with chlorobenzene at 200°–220° under pressure (Fritzsche, D. R.-P. 269543; Eng. P. 9797 of 1913).

αα′-**Dinaphthyl carbonate**, prepared by the interaction of phosgene and sodium α-naphtholate, is a crystalline powder, m.p. 129°–130°, convertible into *α-naphthol-4-sulphonic acid* or a mixture of *α naphthol*-4 : 6- and 4 : 7-*disulphonic acids* by sulphonation (Reverdin, Ber. 1894, 27, 3459; Hochst, D. R.-P. 80888; 80889; Eng. P. 14134, 14135 of 1894).

αα′-**Dinaphthyl sulphite**, m.p. 92°–93°, is obtained by heating α-naphthol in carbon disulphide solution with thionyl chloride in the presence of pyridine (Badische, D. R.-P. 303033).

α-**Naphthyl acetate**, prepared by heating α-naphthol with acetic acid at 200° (Graebe, Annalen, 1881, 209, 151), forms broad needles or tables, m.p. 49° (Miller, Annalen, 1881, 208, 248), is hydrolysed by boiling with water (Schaffer, *l.c.*); gives [α-]*naphthaquinone* on oxidation with chromic acid in acetic acid solution; and when heated with acetic anhydride and zinc chloride is converted into the isomeric 2-*aceto-α-naphthol*, greenish crystals, m.p. 103° (Witt and Braun, Ber. 1914, 47, 3219).

α-Naphtholsulphonic Acids.

Introductory.—The general methods employed in the preparation of α-naphtholsulphonic acids are:—

(1) Sulphonation of α-naphthol;

(2) Exchange of the amino- group in α-naphthylaminesulphonic acids for hydroxyl by the diazo- reaction, or by the bisulphite reaction (*v.* p. 416), or by interaction with water at a high temperature;

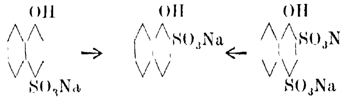
(3) Exchange of chlorine in α-chloronaphthalenesulphonic acids for hydroxyl by fusion with caustic alkali.

(4) Exchange of one sulphonic group in naphthalenepolysulphonic acids for hydroxyl by fusion with caustic alkali.

In addition to these processes, which are of technical importance, others of more limited application or value are known, such as—

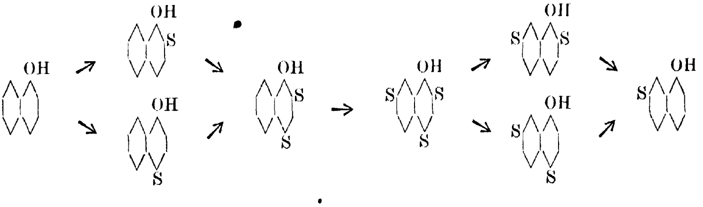
(*a*) The partial hydrolysis of α-naphtholpolysulphonic acids by interaction either with dilute acids at a high temperature or with sodium amalgam in the cold;

(*b*) The change (*cf.* α-naphthylamine-4-sulphonic acid) which sodium α-naphthol-4-sulphonate and 2 : 4-disulphonate undergo when heated at 170°:—



The α-naphtholsulphonic acids and their salts are more soluble and less well-defined than the related α-naphthylaminesulphonic derivatives; they are less easy, therefore, to recognise in or to isolate from mixtures containing them. The zinc salt, although easily soluble, has been used for the purpose of identifying monosulphonic acids, and qualitatively the composition of a sulphonation product can be determined largely by means of nitrous acid (giving rise to *o*- or *p*-nitroso-derivatives), nitric acid (producing naphthol yellows), or diazotised bases (leading to the formation of *o*- or *p*-azo- dyes): reagents which interact with some isomerides but not with others.

The course of the sulphonation of α-naphthol, as traced by the application of these analytical methods, is shown in the scheme—



from which it will be seen that three of the acids owe their formation to partial hydrolysis of the trisulphonic acid—effected by relatively dilute sulphuric acid at the highest temperature employed in these sulphonations.

The scheme also shows that acids containing the SO_3H radicle in the 3-, 5-, or 8- position are not formed by the action of sulphuric acid on α-naphthol. Neither are they formed by the sulphonation of α-naphtholsulphonic acids produced in other ways,[1] and to obtain them recourse must be had to the second general method of preparation in which α-naphthylaminesulphonic acids of the desired orientation are used.

As in the case of the corresponding α-naphthylaminesulphonic acids, it is found that α-naphtholsulphonic acids with a sulphonic group in the 3- position give 1 : 3-diaminonaphthalene derivatives with ammonia; those containing it in the 8- position give *peri*- anhydrides (*sultones*); and those in which it occurs in the 3-, 4-, or 5- position furnish *ortho*-azo- dyes.

α-NAPHTHOLMONOSULPHONIC ACIDS.[2]

(i.) α-**Naphthol-2-sulphonic acid** (*Schaffer's acid*) has not been obtained pure by the sulphonation of α-naphthol. The earliest process for its preparation, by heating α-naphthol with twice its weight of sulphuric acid on a water bath until sulphonation is complete (Schaffer, Annalen, 1869, 152, 293; Darmstadter and Wichelhaus, Eng. P. 89 of 1869), has been shown by Conrad and Fischer (Annalen, 1893, 273, 109), and by Bender (Ber. 1889, 22, 999), to give rise to a product containing much 4-mono- and 2 : 4-di-sulphonic acids.[3] If α-naphthol be heated only for a short time with an equal weight of sulphuric acid at 60°–70°, so that sulphonation is incomplete, the yield is increased from 23 p.c. under Schaffer's conditions to 50 p.c.,[4] and the product can be separated as potassium salt by the addition of potassium chloride to the melt diluted slightly with water (Friedlander and Taussig, Ber. 1897, 30, 1457).

Preparation.—It can be prepared either from α-naphthol by Friedlander and Taussig's method (*l.c.*), or from α-naphthylamine-2-sulphonic acid by the diazo- reaction (Cleve, Ber. 1891, 24, 3476); *or* its sodium salt, in 70–80 p.c. yield, by heating sodium α-naphthol-4-sulphonate or 2 : 4-disulphonate, mixed with twice its weight of naphthalene or paraffin, during 3–4 hours at 160°–170° (Bayer, D. R.-P. 237396; Eng. P. 2355 of 1911).

Salts.—The *acid* forms small rhombic prisms, and differs from its isomerides in being sparingly soluble in dilute mineral acids. The *lead* salt PbA_2+H_2O, scales; *barium* salt $BaA_2+1\frac{1}{2}H_2O$. needles; and *calcium* salt CaA_2+H_2O (?). scales, are sparingly soluble (Cleve, *l.c.*): the *potassium* salt $KA+\frac{1}{2}H_2O$, prisms, is soluble in 37 parts of water at 18°, but almost insoluble in saturated potassium chloride solution (Conrad and Fischer, *l.c.*).

Reactions.—Nitrous acid reacts with it in the cold, forming 4-*nitroso-α-naphthol-2-sulphonic acid*, which does not give a naphthol green with iron salts.[5] With nitric acid it yields 2 : 4-*dinitro-α-naphthol.* By sulphonation it furnishes *α-naphthol-2* : 4-*disulphonic acid.*

Its *acetyl* derivative, obtained by heating the potassium salt with acetic anhydride, is convertible into the *sulphonyl chloride*, m.p. 87·5° (Anschutz and Maxim, Annalen, 1918, 415, 92).

(ii.) α-**Naphthol-3-sulphonic acid** is obtained when naphthalene-1 : 3-disulphonic acid is fused with caustic alkalis at 200°–220° (Badische, D. R.-P. 57910; Eng. P. 9537 of 1890); *or* when diazotised α-naphthylamine-3-sulphonic acid is boiled with 10 p.c. sulphuric acid (Friedländer, Ber. 1895, 28, 1952) or water (Gattermann and Schulze, Ber. 1897, 30, 54); *or* when diazotised 2-amino-8 naphthol-6-sulphonic acid is boiled with alcohol (Badische, *l.c.*; Friedlander and Taussig, Ber. 1897, 30, 1458); *or* when α-naphthol-3 : 8-disulphonic acid is reduced by sodium amalgam in the cold (Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911) or electrolytically (Bayer, D. R.-P. 248527, 251094; Eng P. 28173 of 1911).

Salts.—The *zinc* salt $ZnA_2+8\frac{1}{2}H_2O$ forms long needles and, like the *barium* salt, is easily soluble (Friedländer and Taussig, *l.c.*).

Reactions.—With diazotised aniline, *o*-nitraniline and *p*-nitraniline, it couples respectively in the *ortho*-, in the *para*-, and in both the *ortho*- and the *para*- positions (Gattermann and Schulze, *l.c.*; Gattermann and Liebermann, Annalen, 1912, 393, 214). When heated with ammonia under pressure at 160°–180°, it is converted into 1 : 3-*diaminonaphthalene*, and with aniline and its hydrochloride, at 150°–170°, into *diphenyl*-1 : 3-*diaminonaphthalene.* By digestion with 60 p.c. caustic soda at 180° it yields *o-toluic acid* (Kalle, D. R.-P. 79028; Eng. P. 16559 of 1894).

(iii.) α-**Naphthol-4-sulphonic acid** (*Nevile and Winther's acid*), found in the sulphonation product obtained from α-naphthol by Schäffer's method (*v.* 2-sulphonic acid), can be separated from the 2-sulphonic acid either by converting the product into sodium salt, from which it is extracted by boiling 90 p.c. alcohol (Verein, D. R.-P. 26012; Eng. P. 2237 of 1883), or by precipitation as zinc salt (Friedländer and Taussig, Ber. 1897, 30, 1458).

Preparation.—From α-naphthylamine-4-sulphonic acid it can be prepared by boiling the diazo- compound with 10 p.c. sulphuric acid (Nevile and Winther, Chem. Soc. Trans. 1880, 37, 632; Dahl, D. P. Anm. D. 1486; Eng. P. 2296 of 1883; Erdmann, Annalen, 1888, 247, 341); *or* by heating the sodium salt with 50 p.c.

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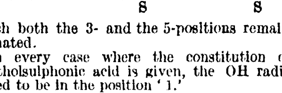
[1] For example, α-naphthol-8-sulphonic acid on sulphonation yields the following products:



in which both the 3- and the 5-positions remain unsulphonated.

[2] In every case where the constitution of an α-naphtholsulphonic acid is given, the OH radicle is supposed to be in the position '1.'

[3] Mixed products also are formed by the methods employed by Claus and Oehler (Ber. 1882, 15, 312; *cf.* Armstrong and Wynne, Chem. Soc. Proc. 1890, 6, 80), by Claus and Knyrim (Ber 1885, 18, 2924), and by Baum (D. P. Anm. B. 4197; Eng. P. 3498 (prov. spec.) of 1883), in which sulphuric acid, chlorosulphonic acid, or anhydro-acid is employed, the methods themselves being valueless (*cf.* Conrad and Fischer, *l.c.*).

[4] According to Holdemann, mercurous sulphate, tried as catalyst, has no influence on the yield by Friedländer and Taussig's method, about equal weights of the 1- and 4-sulphonic acids being recognised in the product (Ber. 1906, 39, 1255).

[5] The production of a naphthol green with iron salts serves to distinguish *ortho*- from *para*-nitroso-derivatives.

caustic soda solution under pressure at 240°–260°, and boiling the solution of the product in water to expel ammonia (Aktienges., D. R.-P. 46307); *or* pure and in almost quantitative yield by the bisulphite method (Bayer, D. R.-P. 109102; Eng. P. 16807 of 1899; *v.* p. 416).

It can also be obtained by digesting α-chloronaphthalene-4-sulphonic acid with 25 p.c. caustic soda solution under pressure at 200°–220° (Oehler, D. R.-P. 77446); *or* by heating α-methoxynaphthalene-4-sulphonic acid with 50 p.c. caustic soda solution under pressure at 240° (Dahl, D. R.-P. 88843); *or* by stirring α-naphthyl carbonate into monohydrate at 10°–20°, pouring the solution on to ice, salting out the disulpho-α-naphthyl carbonate, and boiling this product with water at 60°–70° (Höchst, D. R.-P. 80889; Eng. P. 14135 of 1894; Reverdin, Ber. 1894, 27, 3460).

Salts.—The *acid* and salts are easily soluble. The *zinc* salt ZnA_2+8H_2O forms prisms; the *sodium* salt, which can easily be salted out from solution, forms columnar crystals (Friedlander and Taussig, *l.c.*), is soluble in 90 p.c. alcohol, and gives with ferric chloride a blue or bluish-green colouration (Dahl, *l.c.*; Erdmann, *l.c.*).

Reactions.—The ortho-*azo*- dyes which it furnishes by coupling with diazotised bases are of much technical importance on account of the purity of their shades. Nitrous acid reacts with it in the cold forming *2-nitroso-α-naphthol-4-sulphonic acid*, which gives a *naphthol green* with iron salts. Warmed with dilute nitric acid it is converted into 2 : 4-*dinitro-α-naphthol* (*cf.* Bender, Ber. 1889, 22, 997); digested with ammonium sulphite solution and ammonia at 100°–150° it furnishes *α-naphthylamine-4-sulphonic acid*; sulphonated, it yields successively *α-naphthol-2 : 4-disulphonic acid* (Armstrong, *priv. comm.*) and *α-naphthol-2 : 4 : 7-trisulphonic acid.* Its sodium salt, when heated at 160°–170°, undergoes transformation into sodium *α-naphthol-2-sulphonate.*

(iv.) α-**Naphthol-5-sulphonic acid** (*Cleve's acid*; L-*acid*) is obtained by boiling diazotised α-naphthylamine-5-sulphonic acid with 10 p.c. sulphuric acid (Verein, D. R.-P. 26012; Eng. P 2237 of 1883; *cf.* Cleve, Bull. Soc. chim. 1875, [ii.] 24, 511; Gaess, D. P. Anm. G. 2393; Schöllkopf, Eng. P. 15781 of 1885). It is also formed when sodium naphthalene-1 : 5-disulphonate is fused with caustic soda at 160°–190°; the sparingly soluble sodium α-naphthol-5-sulphonate being isolated by acidifying the aqueous solution of the melt with hydrochloric acid (Ewer & Pick, D. R.-P. 41934); *or* when α-chloronaphthalene-5-sulphonic acid is heated with 8 p.c. caustic soda solution under pressure at 240°–250° (Oehler, D. R.-P. 77446).

Salts.—The *acid* forms a semi-crystalline deliquescent mass (Erdmann, Annalen, 1888, 247, 343); the *zinc* salt $ZnA_2+8\frac{1}{2}H_2O$, easily soluble long needles (Friedlander and Taussig, Ber. 1897, 30, 1460); the *sodium* salt dissolves readily in warm alcohol, and gives with ferric chloride a violet-red colouration (Gaess, *l.c.*).

Reactions.—Diazotised bases couple with it, forming ortho-*azo*- dyes (*cf.* Gesellsch., D R-P. 66838; Gattermann and Schulze, Ber. 1897, 30, 52), but if the diazonium salt contains negative substituents coupling takes place usually in the *para*- position (Gattermann and Liebermann, Annalen, 1912, 393, 211). By nitrous acid in the cold, it is converted into *2-nitroso-α-naphthol-5-sulphonic acid*, which crystallises well, and gives a *naphthol green* with iron salts (Friedländer and Taussig, *l.c.*). On sulphonation with 20 p.c. anhydro-acid below 100°, it gives *α-naphthol-2 : 5-disulphonic acid.* When fused with caustic soda at 220°–260° it yields 1 : 5-*dihydroxynaphthalene*, but with sodamide in naphthalene suspension at 230°, 1-*amino-5-naphthol.*

(v.) α-**Naphthol-6-sulphonic acid** is obtained from α-naphthylamine-6-sulphonic acid either by the diazo- reaction (*cf.* Erdmann and Süvern, Annalen, 1893, 275, 304); or by the bisulphite method (Bayer, D. R.-P. 109102; Eng. P. 16807 of 1899; *v.* p. 416). It is also formed when sodium naphthalene-1 : 6-disulphonate is fused with caustic soda (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 346). Of the properties of this acid little is known.

(vi.) α-**Naphthol-7-sulphonic acid** is probably the chief product when the mixed barium salt from the acids (mainly α-naphthol-2 : 7-, and 4 : 7-disulphonic, and 2 : 4 : 7-trisulphonic acids) obtained by heating α-naphthol with 4 times its weight of sulphuric acid at 130° for an hour, is boiled with hydrochloric or diluted sulphuric acid (Liebmann and Studer, D. P. Anm. L. 4327; Eng. P. 7812 of 1887). In the pure form it can be obtained from α-naphthylamine-7-sulphonic acid by the diazo- reaction, *or* by the bisulphite method (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 347); *or*, from 7-sulpho-1-hydroxy-2-naphthoic acid by heating it with a small quantity of water at 120° (Friedlander and Taussig, Ber. 1897, 30, 1461).

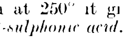
Salts.—The *acid*, a crystalline mass, gives with ferric chloride a brownish-violet colouration and, like the salts, is easily soluble. The *zinc* salt ZnA_2+8H_2O forms radiate groups of needles; the *barium* salt, needles (Friedländer and Taussig, *l.c.*).

Reactions.—Coupled with diazotised *p*-nitraniline in acetic acid solution it gives *monoazo-* and in alkaline solution *disazo-* dyes sensitive to acids (Friedlander and Taussig, *l.c.*; *cf.* Bender, Ber. 1889, 22, 996). Nitrous acid reacts with it, forming a *nitroso-α-naphthol-7-sulphonic acid*, which yields 2 : 4-*dinitro-α-naphthol-7-sulphonic acid* when warmed with dilute nitric acid (Bender, *l.c.*). By the bisulphite reaction it furnishes *α-naphthylamine-7-sulphonic acid.*

(vii.) α-**Naphthol-8-sulphonic acid** (S-*acid*). The product isolated when diazotised α-naphthylamine-8-sulphonic acid is boiled with water or dilute sulphuric acid is not α-naphthol-8-sulphonic acid but *naphthasultone*, the *peri*-anhydride of this acid (Schultz, Ber. 1887, 20, 3162; Erdmann, Annalen, 1888, 247, 344). The acid can be obtained from the sultone by heating it with alcoholic ammonia at 130°, adding lead acetate, and decomposing the precipitated lead salt with hydrogen sulphide (Erdmann, *l.c.*); *or* from α-naphthylamine-8-sulphonic acid either by heating it with water under pressure at 180°–220° (Hochst, D. R.-P. 74644; Eng. P. 14301 of 1892), or by the bisulphite method (*cf.* Bucherer, J. pr. Chem. 1904, [ii.] 70, 347; *v.* p. 416).

Salts.—The *acid* $HA+H_2O$ is crystalline, m.p. 106°–107°, and very soluble. It does not lose its water of crystallisation below 180°, and shows little tendency to pass into the anhydride even in the presence of dehydrating agents. The *potassium* salt KA, scales; the *basic sodium* salt $Na_2A+1\frac{1}{2}H_2O$, small needles; and the *ammonium* salt NH_4A, scales, are easily soluble, and like the acid give with ferric chloride a dark green colouration, changing rapidly to red (Erdmann, *l.c.*).

Reactions.—It couples with diazotised bases forming *azo-* dyes With nitrous acid a sparingly soluble *nitroso-* compound is obtained, which yields 2 : 4-*dinitro-α-naphthol-8-sulphonic acid* when warmed with nitric acid. Fusion with caustic potash at 220° converts it into 1 : 8-*dihydroxynaphthalene*, but with sodamide in naphthalene suspension at 230° into 1-*amino*-8-*naphthol.*

Naphthasultone  $C_{10}H_6{<}{SO_2 \atop O}{>}$, first described as naphtholsulphonic acid S (Schollkopf, D. R.-P. 40571; Eng. P. 15775 of 1885, *v.* 8-sulphonic acid), is obtained almost quantitatively by boiling diazotised α-naphthylamine-8-sulphonic acid with alcohol, water, or dilute sulphuric acid (Karpeles, *cf.* J. Soc. Chem. Ind. 1898, 17, 837). It crystallises from alcohol in large prisms, m.p. 154°, distils above 360° with only slight decomposition, and is almost insoluble in water.

Reactions—It yields salts of α-naphthol-8-sulphonic acid when boiled with aqueous caustic alkalis or alcoholic ammonia, but does not react with these in the cold (Schultz, Ber. 1887, 20, 3162, Erdmann, Annalen, 1888, 247, 345). Sulphonation converts it into *α-naphthol*-4 · 8-*disulphonic acid.*

α-NAPHTHOLDISULPHONIC ACIDS.

(I.) α-**Naphthol**-2 : 4-**disulphonic acid**, formed by the sulphonation of α-naphthol or of α-naphthol-2- or 4-sulphonic acid at temperatures below 100°,[1] is separated from mono- or di-sulphonic acid in the product by removing these either with nitrous acid as sparingly soluble nitroso- compounds, or with diazotised bases as insoluble azo- dyes. When α-naphthol (5 pts.) is heated with sulphuric acid (9 pts.) for 2 hours at 50°, the product consists of the 2 : 4-disulphonic acid mixed with about 5 p.c. (Conrad and Fischer, Annalen, 1893, 273, 105), or about 30 p.c. (Friedlander and Taussig, Ber. 1897, 30; 1457), of α-naphthol-2-sulphonic acid. The acid is also obtained from α-naphthol-2 : 4 : 8-trisulphonic acid by reduction with sodium amalgam (Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911).

Identification.—The *potassium* salt K_2A in solution gives with ferric chloride a deep blue colouration, but is not precipitated by lead acetate or barium chloride, and yields neither azo- dyes nor a nitroso- compound (Conrad and Fischer, *l.c.*).

Reactions.—By nitric acid it is converted into 2 : 4-*dinitro-α-naphthol.* On sulphonation with anhydro-acid, it yields *α-naphthol*-2 : 4 : 7-*trisulphonic acid.* When the potassium salt is heated at 170°–180° (Conrad and Fischer, *l.c.* 111), or the sodium salt, suspended in naphthalene, at 150°–160° the product is the *α-naphthol-2-sulphonate.*

(II.) α-**Naphthol**-2 : 5-**disulphonic acid** is prepared by heating α-naphthol-5-sulphonic acid with sulphuric acid or with 20 p.c. anhydro-acid below 100° (Bayer, D. R.-P. 68344; Eng. P. 3397 of 1890). The *sodium* salt which crystallises in prisms, neither forms a nitroso- derivative with nitrous acid (Bayer, *l.c.*) nor couples with diazotised bases (Gattermann and Schulze, Ber. 1897, 30, 55).

Reaction.—By digestion with 60 p.c. caustic soda solution at 250° it gives 1 : 5-*dihydroxynaphthalene-2-sulphonic acid.*

(III.) α-**Naphthol**-2 : 7-**disulphonic acid** occurs among the products formed when α-naphthol is heated with sulphuric acid at temperatures above 100° for several hours, and is probably the chief constituent of the mixture of acids obtained by sulphonating α-naphthol with 2–3 times its weight of 'about 93 p.c.' sulphuric acid ('65°–66° Bé.') at 125°–130° for about 2 hours (Leonhardt, Eng. P. 11318 of 1887: *cf.* Friedlander and Taussig, Ber. 1897, 30, 1463).[2] A method for isolating the constituents of the mixture has not been described. It can also be obtained[3] from α-naphthylamine 2 · 7-disulphonic acid by the diazo- reaction (*cf.* Reverdin and de la Harpe, Ber 1892, 25, 1405), *or* from α-naphthol 2 . 4 : 7-trisulphonic acid by interaction with sodium amalgam (Friedlander and Lucht, Ber. 1893, 26, 3031).

Identification.—Little is known of the properties of the pure acid It forms a soluble *zinc* salt ZnA (Friedlander and Lucht, *l.c.*); para-*azo-* dyes by coupling with diazotised bases; and a *nitroso-* derivative which does not give a naphthol green with iron salts (Friedlander and Taussig, *l.c.*).

(IV.) α-**Naphthol**-3 . 5-**disulphonic acid**, as an intermediate in the production of 1 : 3-*diamino-naphthalene-5-sulphonic acid*, has been obtained by heating sodium naphthalene-1 : 3 : 5-trisulphonate with caustic soda at 140°–150°, but not described (Kalle, D. R.-P. 94075).

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[1] According to Bender (Ber. 1889, 22, 998), the product obtained by heating α-naphthol with 2.5 times its weight of sulphuric acid at 100°–105° for three hours, contains in addition to the 2 : 4-disulphonic acid about 45 p.c. of a second disulphonic acid, having a sulphonic group in each nucleus, and some trisulphonic acid, its composition being estimated from the results obtained (*a*) by nitration, (*b*) by precipitation with diazotised xylidine.

[2] Bearing in mind the conclusions reached by Bender (Ber. 1889, 22, 998; *cf.* Aktienges., D. R.-P. 45776, Eng. P. 4625 of 1888), and by Friedlander and Taussig (*l.c.*), it is probable that the Patents dealing with the prolonged sulphonation of α-naphthol may be divided into two groups —

(*a*) Those in which anhydro-acid or a relatively large proportion of sulphuric acid is used at 100°, or at temperatures below 100°, leading mainly to the production of α-naphthol-2 : 4-di- and 2 : 4 : 7-trisulphonic acids (*cf.* Seltzer, D. R.-P. 20716; Durand and Huguenin, Eng. P. 2591 (prov. spec.) of 1883; Vignon & Co., Eng. P. 9808 (prov. spec.) of 1884).

(*b*) Those in which a relatively small proportion of sulphuric acid at 100°–130° is used leading to the production of α-naphthol-2 : 7-disulphonic acid mixed with varying proportions of the 4 : 7-di-, and 2 : 4 : 7-tri-sulphonic acids (*cf.* Badische, D. R.-P. 10785; Eng. P. 5305 of 1879, Levinstein, Eng. P. 5692 of 1882; Vignon, D. R.-P. 32291; Eng. P. 6872 of 1884; Leonhardt, Eng. P. 11318 of 1887; Read, Holliday and Sons, Eng. P. 5103 of 1891).

[3] According to Oehler (D. R.-P. 74744), one of the α-naphtholdisulphonic acids obtainable from α-chloronaphthalenedisulphonic acids may have this constitution (*cf.* p. 420, footnote).

(v.) α-**Naphthol**-3 : 6-**disulphonic acid**, obtained when sodium naphthalene-1 : 3 : 6-trisulphonate is heated with 50 p.c. caustic soda solution at 170°–180° (Gurke and Rudolph, D. R.-P. 38281 ; Eng. P. 15716 of 1885), can be prepared from α-naphthylamine-3 : 6-disulphonic acid either by the diazo- reaction (Freund, D. R.-P. 27346 ; Eng. P. 1069 of 1883),[1] or by heating its acid sodium salt with water under pressure at 180° (Cassella, D. P. Anm. C. 4375), *or* from α-naphthol-3 : 6 : 8-trisulphonic acid by reduction with sodium amalgam in the cold (Bayer, D. R.-P. 255724 ; Eng. P. 28172 of 1911).

Identification.—The *acid barium* salt BaH_2A_2 is sparingly soluble ; the *acid sodium* salt NaHA dissolves readily in water or alcohol and gives with ferric chloride a blue colouration (Friedlander and Taussig, Ber. 1897, 30, 1462).

Reactions.—It couples with diazotised bases furnishing ortho-*azo-* dyes. When heated with ammonia at 160°, it is converted into 2-*amino*-4-*naphthol*-7-*sulphonic acid* mixed with 1 : 3-*diaminonaphthalene*-6-*sulphonic acid* or with aniline at 160° into the *diphenyl* derivative of the latter.

(vi.) α-**Naphthol** 3 : 7-**disulphonic acid** can be prepared from α-naphthylamine-3 : 7-disulphonic acid, either by the diazo- reaction (Freund, D. R.-P. 27346, Eng. P. 1069 of 1883),[1] or by heating its acid sodium salt with water under pressure at 180° (Cassella, D. P. Anm. C. 5069) ; *or* from α-naphthol-3 : 5 . 7-trisulphonic acid by boiling with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934).

Reactions.—Of its properties or salts little is known, but it couples with diazotised bases (Freund, *l.c.*). When heated with ammonia at 160°, it yields 2-*amino*-4-*naphthol* 6-*sulphonic acid* mixed with 1 : 3-*diaminonaphthalene*-7-*sulphonic acid* or with aniline at 160° the *diphenyl* derivative of the latter.

(vii.) α-**Naphthol**-3 : 8-**disulphonic acid** (α-*naphthol*-[ε-]*disulphonic acid*) is prepared from α-naphthylamine-3 : 8-disulphonic acid either by heating its acid sodium salt with water under pressure at 180° (Hochst, D. R.-P. 71494 ; Eng. P. 14301 of 1892), or by boiling a solution of its diazo- compound with dilute (6 p.c.) sulphuric acid[2] (Aktienges., D. R.-P. 45776 ; Eng. P. 4625 of 1888 ; Bernthsen, Ber. 1889, 22, 3330).

Identification.—The *sodium* salt Na_2A+6H_2O forms long prisms soluble in about 5·5 parts of cold water, gives with ferric chloride a deep blue colouration, and yields, not a naphthol yellow, but oxidation products with nitric acid (Aktienges., *l.c.* ; Bernthsen, *l.c.*).

Reactions.—It couples with diazotised bases forming ortho-*azo-* dyes. By digestion with 50 p.c. caustic soda solution at 170°–210° it forms 1 : 8-*dihydroxynaphthalene*-3-*sulphonic acid.* On reduction with sodium amalgam it yields α-*naphthol*-3-*sulphonic acid.* When heated with ammonia at 160°-180° it is converted into 1 : 3-*diaminonaphthalene*-8-*sulphonic acid* or with aniline and aniline hydrochloride at 150°–170° into the *diphenyl* derivative of this acid.

Naphthasultone-3-sulphonic acid (*naphthasultonesulphonic acid*-ε ; [ζ-]*naphtholdisulphonic acid*), obtained from the 3 . 8-disulphonic acid by dehydration with sulphuric acid at 100°, or phosphoric oxide or phosphorus pentachloride (Badische, D. R.-P. 55094), forms readily soluble silky needles ; the *barium* salt sparingly soluble long needles ; the *sodium* salt $NaA+3H_2O$ long needles soluble in about 93 parts of cold water. It gives no colouration with ferric chloride, and is readily convertible into α-*naphthol*-3 . 8-*disulphonic acid* by mineral acids or by alkalis (Ewer and Pick, D. R.-P. 52724 ; Badische, *l.c.* ; Bernthsen, *l.c.*).

α-Naphthol-8-sulphonamide-3-sulphonic acid ([ε-] or [ζ-]*naphtholsulphamidesulphonic acid*), $OH\cdot C_{10}H_5(SO_2\cdot NH_2)\cdot SO_3H$, prepared by action of ammonia on the sultone, forms needles, and like the *barium* salt BaA_2+5H_2O, and *sodium* salt $NaA+H_2O$, needles, is moderately soluble; the *sodium ammonium* salt $Na(NH_4)A+H_2O$ ($3H_2O$ in D. R.-P. 53934) forms very soluble small prisms. When boiled with dilute acids it regenerates α-*naphthol*-3 . 8-*disulphonic acid* (Badische, D. R.-P. 53934 ; Bernthsen, *l.c.*). With diazotised bases it couples forming ortho-*azo-* dyes, which when boiled for a short time with alkali hydroxides or carbonates are converted into *peri*-anhydrides $<\begin{smallmatrix}NH\\SO_2\end{smallmatrix}>C_{10}H_4(SO_3H)\cdot N_2\cdot R$, the colour changing from bluish-red to yellow (Bernthsen, Ber. 1890, 23, 3094).

(viii.) α-**Naphthol**-4 : 6-**disulphonic acid** can be prepared from α-naphthylamine-4 : 6-disulphonic acid either by the diazo- reaction (Dahl, D. R.-P. 41957) or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347 ; *v.* p. 416) ; *or* by sulphonating αα′-dinaphthyl carbonate with 5 times its weight of 20 p.c. anhydro-acid at 10°–20°, heating the resulting tetrasulpho-αα′-dinaphthyl carbonates with dilute acid at 60°-70° to eliminate carbon dioxide and separating the less soluble 4 : 7-disulphonic acid by salting out from the more soluble 4 : 6-isomeride (Hochst, D. R.-P. 80888 ; Eng. P. 14134 of 1894).

Reactions.—It yields *azo-* dyes when coupled with diazotised bases, and a *naphthol yellow* when boiled with nitric acid (Dahl, *l.c.*).

(ix.) α-**Naphthol**-4 : 7-**disulphonic acid** occurs in varying amounts in the products obtained by the sulphonation of α-naphthol under conditions which lead also to the formation of the 2 : 7-disulphonic acid (*q.v.* ; *cf.* Friedlander and Taussig, Ber. 1897, 30, 1463). It can be prepared from α-naphthylamine-4 : 7-disulphonic acid either by the diazo- reaction (Dahl, D. R.-P. 41957), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347 ; *v.* p. 416) ; *or* from α-chloronaphthalene-4 : 7-disulphonic acid by digestion with 30 p.c. caustic soda solution at 200°–210° (Oehler, D. R.-P. 74744) ; *or* by eliminating carbon dioxide either from the tetrasulphonation product from αα′-dinaphthyl carbonate (*v.* 4 : 6-disulphonic acid ; Höchst, D. R.-P. 80888 ; Eng. P 14134 of 1894), or from

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[1] In this Patent the product is considered to be a β-naphtholdisulphonic acid solely on account of the fastness to acids shown by the derived azo- dyes, now known to be *ortho*-azo- dyes of the α-series (Cassella, *l.c.*).

[2] If the boiling be stopped directly nitrogen ceases to be evolved, the solution will contain the *peri*-anhydride (sultone), which by continued boiling furnishes the naphtholdisulphonic acid (Bernthsen, *l.c.*).

2 - carboxy - α - naphthol - 4 : 7 - disulphonic acid (Friedländer and Taussig, *l.c.*, 1460; *cf.* Seidler, D. R.-P. 56328) by boiling with dilute acid.

Identification.—The *barium* salt $BaA+4H_2O$ and *sodium* salt Na_2A+4H_2O are crystalline. The sodium salt in solution gives with ferric chloride a blue colouration (Oehler, *l.c.*).

Reactions.—Ortho-*azo*- dyes are obtained by coupling it with diazotised bases. Nitrous acid reacts with it forming a very soluble *nitroso*- compound. Nitric acid converts it, and also the nitroso- compound, into 2 : 4-*dinitro-α-naphthol-7-sulphonic acid.* By the bisulphite method, *α-naphthylamine*-4 : 7-*disulphonic acid* is obtained. When boiled with 65 p.c. sulphuric acid or with hydrochloric acid it yields *α-naphthol*-7-*sulphonic acid.*

(x.) α-**Naphthol**-4 : 8-**disulphonic acid** (*α-naphtholdisulphonic acid* S; *α-naphthol*-[δ-]*disulphonic acid*), obtained when naphthasultone (so-called α-naphtholsulphonic acid S of D. R.-P. 40571) is heated with sulphuric acid at 80°–90° until soluble in water (Schollkopf, D. R.-P. 40571; Eng. P. 15775 of 1885; Bernthsen, Ber. 1890, 23, 3090), is also formed from α-naphthylamine-4 : 8-disulphonic acid either by boiling a solution of its diazo- compound with dilute (6 p.c.) sulphuric acid (Schollkopf, *l.c.*; *cf.* Paul, Z. angew. Chem. 1896, 9, 561), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 69, 80; *v.* p. 416).

Identification.—The *barium* salt is sparingly soluble; the *sodium* salt Na_2A+H_2O forms very soluble scales (Aktienges., D. R.-P. 45776; Eng. P. 4625 of 1888) and with ferric chloride gives a deep blue colouration (Bernthsen, *l.c.*).

Reactions.—It couples with diazotised bases forming ortho-*azo*- dyes. Nitrous acid reacts with it forming the 2-*nitroso*- derivative (Dressel and Kothe, Ber. 1894, 27, 2145). Nitric acid converts it, and also the nitroso- derivative, into 2 : 4-*dinitro-α-naphthol-8-sulphonic acid.* By the bisulphite reaction it yields *α-naphthylamine*-4 : 8-*disulphonic acid.* On dehydration it gives *naphthasultone-4-sulphonic acid*, but when sulphonated with 25 p.c. anhydro-acid below 100°, *α-naphthol*-2 : 4 : 8-*trisulphonic acid* is the product. Fusion with caustic soda at 250° converts it into 1 : 8 - *dihydroxynaphthalene* - 4 - *sulphonic acid.*

Naphthasultone-4-sulphonic acid (*naphthasultonesulphonic acid*-δ), obtained from the 4 : 8-disulphonic acid by dehydration with 5 p.c. anhydro-acid in the cold, forms an easily soluble *barium* salt. The *sodium* salt ($+3H_2O$), in moderately soluble scales, is converted readily into the *α-naphthol*-4 : 8-*disulphonate* by alkalis or alkali carbonates in the cold, or into the *acid* by boiling with 5 p.c. sulphuric acid, or prolonged boiling with water. It gives neither a colouration with ferric chloride nor azo- dyes with diazotised bases (Bernthsen, *l.c.*; Badische, D. R.-P. 57388).

α-Naphthol-8-sulphonamide-4-sulphonic acid ([δ-]*acid*) is precipitated by hydrochloric acid from a solution of the sultonesulphonate in ammonia as the crystalline *sodium* salt $OH{\cdot}C_{10}H_5(SO_2NH_2){\cdot}SO_3Na+2H_2O$ which separates in rhomb-like scales and regenerates the *sultone* or *α-naphthol*-4 : 8-*disulphonic acid* when boiled with dilute acids (Badische, D. R.-P. 57856; Bernthsen, *l.c.*). It couples with diazotised bases forming ortho-*azo*- dyes which closely resemble those obtained from the 8-sulphonamide-3-sulphonic acid (*cf.* Badische, D. R.-P. 60777, 64065; Geigy, D. R.-P. 139287).

(xi.) α-**Naphthol**-5 : 7-**disulphonic acid** has not been described, but is mentioned in connexion with the bisulphite reaction as producible from and convertible into *α-naphthylamine*-5 : 7-*disulphonic acid* (Badische, D. R.-P. 115335, 117471; Eng. P. 1387 of 1900).

(xii.) α-**Naphthol**-5 : 8-**disulphonic acid,** which is obtained from α-naphthylamine-5 : 8-disulphonic acid by the diazo- reaction, the *sultone* first formed being converted by alkali into the naphtholdisulphonic acid (Bayer, D. R.-P. 70857), regenerates the *amino*- acid by the bisulphite reaction (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900).

Naphthasultone-5-sulphonic acid forms a *sodium* salt $NaA+\frac{1}{2}H_2O$ in moderately soluble needles (Gattermann, Ber. 1899, 32, 1158), and, like the disulphonic acid, when digested with 40 p.c. caustic soda solution under pressure at 170°–200° yields 1 : 8-*dihydroxynaphthalene*-4-*sulphonic acid* (Bayer, D. R.-P. 80667; Eng. P. 1227 of 1894).

(xiii.) α-**Naphthol**-6 : 8-**disulphonic acid** has been prepared from α-naphthylamine-6 : 8-disulphonic acid either by the diazo- reaction, the sultone first formed being converted into the naphtholdisulphonic acid by alkali (Bayer, D. R.-P. 75084) or by the bisulphite reaction (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347). It is also formed when α-naphthylamine-4 : 6 : 8-trisulphonic acid (Kalle, D. R.-P. 82563), or α-naphthol-4 : 6 : 8-trisulphonic acid (Kalle, D. P. Anm. K. 11397) is heated with dilute (3 p.c.) acid at 180°–200°. The *acid sodium* salt forms easily soluble short needles, and with ferric chloride gives a fleeting green colouration.

Reactions.—It couples with diazotised bases forming *azo*- dyes. With nitrous acid, it yields a *nitroso*- derivative which is not convertible into a naphthol yellow by nitric acid (Kalle, *l.c.*). By the bisulphite method it is converted into *α-naphthylamine*-6 : 8-*disulphonic acid.* When digested with 50 p.c. caustic soda solution at 170°–210°, it gives 1 : 8-*dihydroxynaphthalene*-3-*sulphonic acid.*

The corresponding naphthasultone-6-sulphonic and α-naphthol-8-sulphonamide-6-sulphonic acids have not been fully characterised (Bayer, *l.c.*).

α-Naphtholtrisulphonic Acids.

(i.) α-**Naphthol**-2 : 4 : 7-**trisulphonic acid** is the chief product of the sulphonation of α-naphthol either with 25 p.c. anhydro- acid at 100°–110° or with 45 p.c. anhydro- acid at 40°–50° (Badische, D. R.-P. 10785; Eng. P. 5305 of 1879),[1] and can be isolated by means of the characteristic barium salt (Friedländer and Taussig, Ber. 1897, 30, 1463). It is also obtained when diazotised α-naphthylamine-2 : 4 : 7-trisulphonic acid is boiled with acidified water (*cf.* Höchst, D. R.-P. 22545; Eng. P. 2178 of

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[1] The acid formed by heating α-naphthol with three times its weight of sulphuric acid at 110°–115° for twelve to fifteen hours (Badische, *l.c.*), and serving as a source of naphthol yellow S (v. 2 : 4-dinitro-α-naphthol-7-sulphonic acid), would probably contain a large proportion of the 2 : 7- and 4 : 7-disulphonic acids (*cf.* p. 470, footnote 2).

1882), *or* when a-chloronaphthalene-2 : 4 : 7-trisulphonic acid is heated with 12 p.c. caustic soda solution under pressure at 150° (Oehler, D. R.-P. 77996).

Identification.—The *barium* salt $Ba_3A_2+3H_2O$ in glistening minute crystals, is almost insoluble when once separated from water; the other salts are easily soluble (Friedländer and Taussig, *l.c.*). The *sodium* salt gives a blue colouration with ferric chloride, but yields neither azo- dyes nor a nitroso- compound.

Reactions.—Nitric acid converts it into 2 : 4-*dinitro-a-naphthol-7-sulphonic acid.* On fusion with caustic alkali, it yields 1 : 7-*dihydroxynaphthalenedisulphonic acid.* By desulphonation with sodium amalgam in the cold it gives *a-naphthol-2 : 7-disulphonic acid*, but when heated with hydrochloric acid or 66 p.c. sulphuric acid, *a-naphthol-7-sulphonic acid* is the product.

(ii.) a-**Naphthol**-2 : 4 : 8-**trisulphonic acid** has been prepared by sulphonating a-naphthol-4 : 8-disulphonic acid or its sultone with 25 p.c. anhydro- acid below 100° (Bayer, D. P. Anm. F. 4569 ; Eng. P. 3397 of 1890 ; Dressel and Kothe, Ber. 1894, 27, 2143).

Identification.—The *sodium* salt ($+1\frac{1}{2}H_2O$) is a readily soluble crystalline powder, shows green fluorescence in solution, gives with ferric chloride a blue colouration, and does not couple with diazotised bases (Dressel and Kothe, *l.c.*).

Reactions.—With nitro-sulphuric acid at 20° it gives 2 : 4-*dinitro-a-naphthol-8-sulphonic acid.* On desulphonation with sodium amalgam in the cold, it yields *a-naphthol-2 : 4-disulphonic acid.* By fusion with caustic soda at 210° it is converted into 1 : 8-*dihydroxynaphthalene-2 : 4-disulphonic acid.*

(iii.) a-**Naphthol**-3 : 5 : 7-**trisulphonic acid** can be obtained either from naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid by digestion with 15 p.c. caustic soda solution under pressure at 180° (Bayer, D. R.-P. 79054 ; Eng. P. 25074 of 1893), or from a-naphthylamine-3 : 5 : 7-trisulphonic acid by the diazo- reaction (Kalle, D. P. Anm. K. 12732).

Reactions.—In neutral or alkaline solution it combines with tetrazo- derivatives of the diphenyl series forming *salts* (Bayer, D. R.-P. 92169 ; Eng. P. 8995 of 1895). Boiled with zinc-dust and dilute caustic soda solution, it gives *a-naphthol-3 : 7-disulphonic acid.* When heated with ammonia at 160°–180° it is converted into 1 : 3-*diaminonaphthalene-5 : 7-disulphonic acid.* By digestion with 50 p.c. caustic soda solution at 150°–160°, it yields 1 . 5-*dihydroxynaphthalene-3 : 7-disulphonic acid* but with 60 p.c. solution at 200°, a mixture of this acid with 1 : 3-*dihydroxynaphthalene-5 : 7-disulphonic acid.*

(iv.) a-**Naphthol**-3 : 6 : 8-**trisulphonic acid** is formed from a-naphthylamine-3 : 6 : 8-trisulphonic acid either by the diazo- reaction, the sultone being an intermediate product (Koch, D. R.-P. 56058; Eng. P. 9258 of 1890), *or* by heating it with water under pressure at 180°–250° (Höchst, D. R.-P. 71495; Eng. P. 14301 of 1892).

Reactions.—It couples with diazotised bases forming *azo-* dyes. On desulphonation by sodium amalgam in the cold, it gives *a-naphthol-3 : 6-disulphonic acid.* When heated with ammonia at 160°-180° it is converted into 1 : 3-*diaminonaphthalene-6 : 8-disulphonic acid* or with aniline at 150°–170° into the *diphenyl* derivative of this acid. By digestion with 60 p.c. caustic soda solution at 170°–220° it yields 1 : 8-*dihydroxynaphthalene-3 : 6-disulphonic acid* (chromotrope acid).

Its sultone gives yellow solutions with alkalis. Dissolved in ammonia, the sodium sultonesulphonate when mixed with hydrochloric acid yields sodium a-naphthol-8-sulphonamide-3 : 6-disulphonate (Koch, *l.c.*; Hochst, D. R.-P. 69518), which couples with diazotised bases forming *azo-* dyes.

(v.) a-**Naphthol**-4 : 6 : 8-**trisulphonic acid** has been obtained from a-naphthylamine-4 : 6 : 8-trisulphonic acid either by the diazo- reaction, the sultone formed being dissolved in alkali (Bayer, D. P. Anm. F. 7006 ; *cf.* D. R.-P. 80741 ; Eng. P. 17141c of 1893), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347 ; *v.* p. 416).

Reactions.—By hydrolysis with 3 p.c. hydrochloric acid at 160°–200°, it yields *a-naphthol-6 : 8-disulphonic acid.* Digestion with 70 p.c. caustic soda solution at 170°–190° converts it into 1 : 8-*dihydroxynaphthalene-3 : 5-disulphonic acid.*

Its sultone is easily soluble, forming colourless non-fluorescent solutions which with alkalis become deep yellow; the corresponding a-naphthol-8-sulphonamide-4 : 6-disulphonic acid couples with diazotised bases giving ortho-*azo-* dyes.

CHLORO-a-NAPHTHOLS.

Introductory.—By chlorination a-naphthol gives rise only to homonucleal derivatives. When the operation is carried out by passing chlorine into a cooled acetic acid solution of the naphthol, substitution occurs with the production of 2 : 4-*dichloro-a-naphthol* (Cleve, Ber. 1888, 21, 891), followed by the formation of the additive compounds *trichloro-a-keto-* and *pentachloro-a-ketonaphthalene* (Zincke and Kegel, Ber. 1888, 21, 1030).

4-**Chloro**-a-**naphthol** can be obtained by chlorinating either a-naphthyl carbonate (Reverdin and Kauffmann, Ber. 1895, 28, 3051), or a-naphthyl toluene-*p*-sulphonate in carbon tetrachloride solution (Aktienges., D. R.-P. 240038). It can also be prepared from a-naphthol by employing sulphuryl chloride as the chlorinating agent (Kast, Ber. 1911, 44, 1337 ; Höchst, D. P. Anm. F. 29600) ; but when the naphthol, dissolved in alkali, is chlorinated by hypochlorous acid (Kalle, D. R.-P. 167458) the product is not pure (*cf.* King, Chem. Soc. Proc. 1911, 27, 266). It sublimes in long needles, m.p. 117°–118°, dissolves readily in alcohol or benzene, gives a blue precipitate with ferric chloride and couples with diazotised bases.

Chloro-a-naphtholsulphonic acids.—Four, namely, the 6- and 7-*chloro-a-naphthol-3-sulphonic acids*, the 6-*chloro-a-naphthol-3* : 5- and the 8-*chloro-a-naphthol-3 : 6-disulphonic acids*, formed from the corresponding aminonaphthol-mono- and di-sulphonic acids by the Sandmeyer reaction, have been used for coupling with diazotised dehydrothiotoluidine in the production of *ortho*-azo- dyes (Bayer, D. R.-P. 96768 ; Eng. P. 9441 of 1894).

8-Chloro-α-naphthol-3 : 6-disulphonic acid, *obtained also* by heating 8-chloro-α-naphthylamine-3 : 6-disulphonic acid with dilute sulphuric acid under pressure (Badische, D. R.-P. 147852), is a crystalline, deliquescent substance. Its *acid barium* salt, $BaH_2A_2+6H_2O$, crystallises in needles; *acid potassium* salt, in scales; and *acid sodium* salt, in needles. The normal salts dissolve easily, yielding non-fluorescent solutions, which with ferric chloride give a dark green colouration (Cassella, D. R.-P. 79055; Eng. P. 1920 of 1894). Compared with the azo- dyes from α-naphthol-3 : 6-disulphonic acid, those from this *peri*-chloro- acid are much bluer in shade and of enhanced fastness (Cassella, *l.c.*; D. R.-P. 82285; 99227).

NITROSO-α-NAPHTHOLS.

(*v. Naphthaquinoneoximes.*)

NITRO-α-NAPHTHOLS.

Introductory.—Nitro-α-naphthols are obtained, not from α-naphthol by direct nitration, as the yield is unsatisfactory owing to the production of tars, but from naphtholsulphonic acids, nitrosonaphthols, or nitrosonaphtholsulphonic acids, containing the nitroso- group, or at least one sulphonic group, in the same nucleus as the hydroxyl radicle. An alternative method from α-chloronitronaphthalenes is known, and, although it has no technical importance, four nitro-α-naphthols have been prepared by its aid, *viz.* the 4-mono-, the 2 : 4-di-, and the 2 : 4 : 5- and 2 : 4 : 8-trinitro-α-naphthols, each of which, save the last, regenerates the corresponding α-chloronitronaphthalene by interaction with toluene-*p*-sulphonyl chloride and diethylaniline (*cf.* Rindl, Chem. Soc. Trans. 1913, 103, 1911).

The nitro-α-naphthols containing a nitro-group in the *ortho*- position relatively to the hydroxyl radicle dye wool and silk in various shades of yellow.

(i.) 2-**Nitro-α-naphthol** is obtained by boiling acetyl-2-nitro-α-naphthylamine with aqueous caustic soda (Liebermann and Dittler, Annalen, 1876, 183, 246; Lellmann and Remy, Ber. 1886, 19, 802), *or* by hydrolysing 2-nitro-α-ethoxynaphthalene-4-sulphonic acid (Witt and Schneider, Ber. 1901, 34, 3189); *or*, together with 2 : 4-dinitro-α-naphthol, by boiling α-diazonaphthalene sulphate with nitric acid in mol. prop. (Noelting and Wild, Ber. 1885, 18, 1339); *or*, better, by suspending 2-nitroso-α-naphthol (5 g.) in water (60 c.c.), adding nitric acid of sp.gr. 1·3 (45 c.c.) in the cold, and, after 15 hours, distilling the product with steam (Grandmougin and Michel, Ber. 1892, 25, 973).

Properties.—It crystallises in greenish-yellow scales, m.p. 128°, dissolves sparingly in dilute alcohol, but less readily in water, and resembles *o*-nitrophenol in being volatile with steam and in forming dark red salts. Its *acetate* forms bright-yellow needles, m.p. 118° (Grandmougin and Michel, *l.c.*), and *ethyl ether*, bright yellow needles, m.p. 84° (Heermann, J. pr. Chem. 1891, [ii.] 44, 240).

(ii.) 4-**Nitro-α-naphthol** (*French yellow; Campobello yellow; Chryseic acid*) can be prepared by boiling acetyl-4-nitro-α-naphthylamine with aqueous caustic soda (Andreoni and Biedermann, Ber. 1873, 6, 343; *cf.* Lellmann and Remy, Ber. 1886, 19, 796); and is formed when bis-4-nitro-α-naphthyl carbonate, m.p. 212°, is heated with alcoholic potash (Reverdin and Kauffmann, Ber. 1895, 28, 3050); *or* when 4-nitro-α-chloronaphthalene is heated with aqueous sodium carbonate under pressure at 150°–155° (Griesheim, D. R.-P. 117731; Eng. P. 7692 of 1900).

Properties.—It crystallises from hot water in golden-yellow needles, m.p. 164°, is readily soluble in alcohol or acetic acid, and, like *p*-nitrophenol, does not volatilise with steam. The salts (Biedermann, Ber. 1873, 6, 1118) are orange-red to dark-red in colour, and dissolve readily in water; the *sodium* salt $NaA+2H_2O$, carmine-red needles, was formerly used as a yellow dye for silk or wool. The *methyl ether*, m.p. 85°–86° (Griesheim, *l.c.*), and *ethyl ether*, needles, m.p. 116°–117° (Heermann, *l.c.*; Witt and Schneider, *l.c.*) have been described. On nitration it yields 2 : 4-*dinitro-α-naphthol.*

(iii.) 5-**Nitro-α-naphthol**, obtained from 5-nitro-α-naphthylamine sulphate by the diazo-reaction, separates from hot water in dark-yellow crystals, m.p. 165°, gives an *acetate*, needles, m.p. 114°, and *benzoate*, needles, m.p. 109°; couples with diazotised bases; and with nitrous acid yields 5-*nitro-4-nitroso-α-naphthol* (Kaufler and Brauer, Ber. 1907, 40, 3271).

DINITRO-α-NAPHTHOLS.

(i.) 2 : 4-**Dinitro-α-naphthol** (*Martius yellow, Manchester yellow, Naphthalene yellow, Naphthol yellow*) is obtained by the action of nitric acid on α-naphthol (Dale, Caro and Martius. Eng. P. 2785 of 1864; Martius, Zeitsch. Chem. 1868, [ii.] 4, 80), 2-nitroso- or 4-nitroso-α-naphthol (Fuchs, Ber. 1875, 8, 629), 2-nitro- or 4-nitro-α-naphthol (Liebermann and Dittler, Annalen, 1876, 183, 249), and on α-naphthol-2-sulphonic acid (Darmstadter and Wichelhaus, Eng. P. 89 of 1869; Annalen, 1869, 152, 299), α-naphthol-4-sulphonic acid (Cleve, Förhandl. 1876, 7, 40), α-naphthol-2 : 4-disulphonic acid (Bender, Ber. 1889, 22, 996); or (but mixed with 2-nitro- and 4-nitro-α-naphthol) α-ethoxynaphthalene-4-sulphonic acid (Witt and Schneider, Ber. 1901, 34, 2186). It is also formed when α-naphthylamine is heated with concentrated nitric acid (Balló, Ber. 1870, 3, 288); *or* when acetyl-2 : 4-dinitro-α-naphthylamine is boiled with aqueous caustic soda (Liebermann and Hammerschlag, Annalen, 1876, 183, 273); *or* when nitrous fumes are led into an ethereal solution of α-naphthol at 0° (Schmidt, Ber. 1900, 23, 3245).

Preparation.—Either α-naphthol-2 : 4-disulphonic acid, made by sulphonating α-naphthol with twice its weight of sulphuric acid below 50°, is heated with dilute nitric acid at 100°, or the two α-naphtholmonosulphonic acids, formed when α-naphthol is sulphonated under Schaffer's conditions, are converted into their nitroso-derivatives by interaction with sodium nitrite and sulphuric acid in the cold, and the mixed product is then warmed with nitric acid (*cf.* Bender, *l.c.* footnote).

Properties.—It crystallises from alcohol in citron-yellow needles, m.p. 138°, does not volatilise with steam, is almost insoluble in water, and dissolves only sparingly in alcohol, ether, or benzene. It is sufficiently acidic to expel carbon dioxide from carbonates, and it forms soluble, orange-coloured salts (Martius, *l.c.*; for salts with organic bases *cf.* Norton and Lowenstein, J. Amer. Chem. Soc. 1897, 19, 923; Korczyński, Ber. 1909, 42, 174). The *sodium* salt $NaA+H_2O$, *ammonium* salt NH_4A+H_2O, and *calcium* salt CaA_2+6H_2O, crystallise in needles (Martius, *l.c.*), and were used formerly as golden-yellow dyes for silk and wool. Dinitro-α-naphthol, however, has little affinity for the fibre, being removed from it either by volatilisation or by washing.

Reactions.—Nitration in the presence of much sulphuric acid at temperatures below 50° converts it into a mixture of 2 : 4 : 5-*trinitro-* with 2 : 4 : 7-*trinitro-α-naphthol.* Prolonged boiling with concentrated nitric acid oxidises it to *phthalic* and *oxalic acids* (Martius, *l.c.*). By digestion with alcoholic ammonia at 190°–200° it yields 2 : 4-*dinitro-α-naphthylamine.* When heated with potassium cyanide in hot alcoholic solution, *naphthylpurpuric acid* is formed (Sommaruga, Annalen, 1871, 157, 328), and with toluene-*p*-sulphonyl chloride and diethylaniline 4-*chloro*-1 : 3-*dinitronaphthalene* is obtained (Ullmann and Bruck, Ber. 1908, 41, 3932.

(ii.) 4 : 5-**Dinitro**-α-**naphthol,** formed when 5-nitro-4-nitroso-α-naphthol is oxidised by alkaline potassium ferricyanide solution, crystallises in yellow needles, m.p 230°, dissolves only sparingly in water, and has only feeble dyeing properties (Friedländer, Ber. 1899, 32, 3529). The *methyl* ether, m.p 216°, and *ethyl* ether, scales, m p. 182°, have been described (Ullmann and Consonno, Ber. 1902, 35, 2808).

(iii.) 4 : 8-**Dinitro**-α-**naphthol,** obtained similarly from 8-nitro-4-nitroso-α-naphthol, has m.p. 135°, but otherwise resembles the 4 : 5- derivative in properties (Friedlander, *l.c.*).

TRINITRO-α-NAPHTHOLS.

(i.) 2 : 4 : 5-**Trinitro**-α-**naphthol** (*Naphthopicric acid*) is formed when 5-nitro-4-nitroso-α-naphthol is warmed with dilute nitric acid (Graebe, Ber. 1899, 32, 2878, Graebe and Oeser, Annalen, 1904, 335, 147; Friedlander and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339); *or*, mixed with the 2 : 4 : 7-trinitro- derivative, when 2 : 4-dinitro-α-naphthol is nitrated in the cold with nitrosulphuric acid (Kehrmann and Haberkant, Ber. 1898, 31, 2421; *cf.* Diehl and Merz, Ber. 1878, 11, 1662).

Properties.—It forms needles, m.p. 190°, and its *potassium* salt $KA+H_2O$, needles, easily soluble in hot, but only sparingly so in cold water (Kehrmann and Steiner, Ber. 1900, 33, 3281). It is a strong acid, dyes wool yellow, yields 3-*nitrophthalic acid* on oxidation, and gives 4-*chloro*-1 : 3 : 8-*trinitronaphthalene* when heated with toluene-*p*-sulphonyl chloride and diethylaniline (Rindl, Chem. Soc. Trans. 1913, 103, 1914).

(ii.) 2 : 4 : 7-**Trinitro**-α-**naphthol** is the more soluble product obtained when 2 : 4-dinitro-α-naphthol is nitrated in the cold with nitrosulphuric acid (Kehrmann and Haberkant, *l.c.*), and is freed from the 2 : 4 : 5- compound by conversion into the sparingly soluble sodium salt (Kehrmann and Steiner, Ber. 1900, 33, 3286).

Properties.—It forms yellow needles, m.p. 145°, but, from benzene or acetic acid, prisms containing solvent which effloresce in the air. On oxidation it yields 4-*nitrophthalic acid* (Kehrmann and Haberkant, *l.c.*). The *potassium* salt is easily, but the *sodium* salt, yellow needles, only sparingly soluble in water.

(iii.) 2 : 4 : 8-**Trinitro**-α-**naphthol,** obtained by mixing 8-nitro-4-nitroso-α-naphthol with 50 p.c. nitric acid in the cold (Graebe and Oeser, Annalen, 1904, 335, 156; Friedlander and Scherzer, *l.c.*), forms yellow prisms, m.p. 175°, and dyes wool yellow. The *potassium* salt KA, crystallises well (Friedlander, Ber. 1899, 32, 3530).

(iv.) 4 : 5 : 7- (or 4 : 6 : 8-) Trinitro-α-naphthol has not been isolated, but its *methyl ether* is formed by the interaction of 1 : 3 : 5 : 8-tetranitronaphthalene and sodium methoxide. This ether crystallises in yellow needles, m.p. 186°, and on oxidation yields 3 : 5-*dinitrophthalic acid* (Will, Ber. 1895, 28, 372).

TETRANITRO-α-NAPHTHOL.

2 : 4 : 5 : 7-**Tetranitro**-α-**naphthol** (*Heliochrysin*) is obtained by digesting tetranitro-α-bromonaphthalene (m.p. 170·5°) with warm, concentrated aqueous sodium carbonate (Höchst, D. R.-P. 14954; Eng. P. 5327 of 1880; Merz and Weith, Ber. 1882, 15, 2714). It crystallises in yellow scales, m.p. 180°, and forms reddish-yellow salts, which dissolve only sparingly in water. The *potassium* salt $KA+1\frac{1}{2}H_2O$, prisms, is soluble in 340 parts, and the *sodium* salt $NaA+2H_2O$, scales, in about 94 parts of water at 19°. It dyes silk and wool golden-yellow, but has no technical value.

NITRO-α-NAPHTHOLSULPHONIC ACIDS.

(i.) 2-**Nitro**-α-**naphthol-4-sulphonic acid** can be obtained from the corresponding ethyl ether by hydrolysis with caustic potash solution. The *basic barium* salt $BaA+H_2O$ is very sparingly soluble; the yellow *potassium* and orange *basic potassium* salts form needles easily soluble in water. When its salts are heated with hydrochloric acid under pressure at 150°–160° 2-*nitro-α-naphthol* is obtained (Witt and Schneider, Ber. 1901, 34, 3189).

(ii.) 2-**Nitro**-α-**naphthol-7-sulphonic acid,** formed from diazotised 2-nitro-4-amino-α-naphthol-7-sulphonic acid (*v.* 2 : 4-dinitro-α-naphthol-7-sulphonic acid) by means of copper powder, crystallises with 1 mol. H_2O in yellow needles, and its *copper* salt CuA_2+5H_2O in greenish-yellow needles. On reduction it yields 2-*amino-α-naphthol-7-sulphonic acid* (Finger, J. pr. Chem. 1909, [ii.] 79, 441).

(iii.) 2 : 4-**Dinitro**-α-**naphthol-7-sulphonic acid** (*naphthol yellow S*; *acid yellow S*) is formed by nitration of α-naphthol-7-sulphonic acid (Liebmann and Studer, Eng. P. 7812 of 1887; *cf.* Bender, Ber. 1889, 22, 996), *or* of α-naphthol-4 : 7-disulphonic acid (Dahl, D. R.-P. 41957), *or* of a mixture of α-naphthol-2 : 7- and 4 : 7-disulphonic acids (Seltzer, D. R.-P. 20716; Levinstein, Eng. P. 5692 of 1882; L. Vignon & Co., Eng. P. 9808 (prov. spec.) of 1884; Leonhardt, Eng. P. 11318 of 1887), *or* of α-naphthol-2 : 4 : 7-trisulphonic acid (Badische, D. R.-P. 10785; Eng. P. 5305 of 1879; *cf.* Lauterbach, Ber. 1881, 14, 2028; Hochst, D. R.-P. 22545; Eng. P. 2178 of 1882), *or* of α-methoxynaphthalenedisulphonic acid (Dahl, Eng. P. 1964 of 1883).

Preparation.—(1) To the solution obtained by diluting the trisulphonation melt from α-naphthol (10 kilos.) with water to 100 litres nitric acid of sp.gr. 1·38 (25 kilos.) is added at such a rate that the temperature does not exceed 50°, and the reaction completed either at 50° or by allowing the mixture to remain in the cold for 12 hours. From the solution, dinitro-α-naphthol-sulphonic acid separates in needles, the mother liquors containing other nitration products, of which nothing definite is known (Badische, *l.c.*).

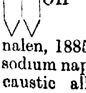
(2) The mixed α-naphtholdisulphonic acids of Leonhardt's Eng. P. 11318, after conversion into nitroso- compounds by means of sodium nitrite, are nitrated at 50° with nitric acid, also in the proportion of 25 kilos. to every 10 kilos. of α-naphthol sulphonated (Leonhardt, *l.c.*).

Salts.—The *acid* crystallises from hydrochloric acid in yellow needles. The *barium* and *basic potassium* K_2A salts are very sparingly soluble; the *acid potassium* KA, *basic sodium* Na_2A, and *ammonium* salts are readily soluble in water and are orange-yellow (Lauterbach, *l.c.*). It is a strong acid, has considerable tinctorial power, is used as a yellow dye for wool, and, unlike 2 : 4-dinitro-α-naphthol, does not volatilise from the fibre and is not poisonous.

Reactions.—By oxidation with nitric acid of sp.gr. 1·33 it is converted into *β-sulphophthalic acid* (Graebe, Ber. 1885, 18, 510; Rée, Chem. Soc. Trans. 1886, 49, 511). When reduced with stannous chloride and hydrochloric acid it yields 2-*nitro*-4-*amino*-α-*naphthol*-7-*sulphonic acid* (Lauterbach, *l.c.*; Finger, J. pr. Chem. 1909, [ii.] 79, 441); but in ammoniacal solution with sodium sulphide gives the isomeric 4-*nitro*-2-*amino*-α-*naphthol*-7-*sulphonic acid* (Gesellsch., D. R.-P. 189513; Eng. P. 7535 of 1906).

(iv.) 2 : 4-**Dinitro**-α-**naphthol**-8-**sulphonic acid** (*brilliant yellow*) is formed when the nitroso-derivative of sodium α-naphthol-8-sulphonate in dilute sulphuric acid solution, is mixed with nitre in the cold, the reaction being completed on a water bath (Schöllkopf, D. R.-P. 42304); *or* when sodium α-naphthol-4 : 8-disulphonate in aqueous solution is heated with dilute nitric acid at 60°–70° (Schollkopf, D. R.-P. 40571; Eng. P. 15775 of 1885); or its nitroso- derivative is boiled with nitric acid (Karpeles, *cf.* J. Soc. Chem. Ind. 1898, 17, 837); *or* when sodium α-naphthol-2 : 4 : 8-trisulphonate, dissolved in sulphuric acid, is mixed with nitrosulphuric acid at 20° (Dressel and Kothe, Ber. 1894, 27, 2145).

Properties.—The *potassium* salt $KA + H_2O$ (Karpeles, *l.c.*), and the *sodium* salt NaA (Dressel and Kothe, *l.c.*), form sparingly soluble yellow needles, and in an acid bath dye silk and wool a more orange shade than that produced with the isomeric 7-sulphonic acid. As a dyestuff it has no technical value.



(ii.) β-**Naphthol** occurs in very small amount in the coal tar fractions of high boiling-point (Schulze, Annalen, 1885, 227, 150), but is always made from sodium naphthalene-β-sulphonate by fusion with caustic alkali (Schäffer, Annalen, 1869, 152, 281).

Preparation.—A melt of caustic soda (10 pts.) with water (2 pts.) is heated at 270° until frothing stops; sodium naphthalene-β-sulphonate (15–25 pts.) is then stirred in gradually while the temperature is raised slowly to 300°–310°, at which the fusion is completed. The liquid naphtholate, containing sodium sulphite in suspension, is dissolved in the minimum amount of water, the solution neutralised by 50 p.c. sulphuric acid, heated to boiling and acidified with sufficient 50 p.c. sulphuric acid to liberate about 85 p.c. of the naphthol, which when cold is removed by filtration. By this means β-naphthol, free from α-naphthol (arising from α-sulphonate present as impurity in the β-sulphonate used), is obtained, while from the filtrate after dilution the remainder of the β-naphthol may be separated by the addition of more acid, the α-naphthol remaining in solution. When dry, the β-naphthol is purified by distillation in a vacuum (*cf.* Cain, Intermediates, 2nd ed. 213; Levinstein, Eng. P. 2300 of 1883).

To avoid the formation of oxidation products which occurs when sulphonic acids are fused with caustic alkali in open vessels (*cf.* Boswell and Dickson, J. Amer. Chem. Soc. 1918, 40, 1787), sodium naphthalene-β-sulphonate (46 pts.) may be heated with caustic soda solution of sp.gr. 1·384 (50 pts.) in an autoclave at 300°–330° for 10–12 hours (Aktienges., D. P. Anm. A. 24027; *cf.* J. Soc. Chem. Ind. 1914, 33, 955); *or* with 10 p.c. caustic soda solution at 300° for 30 hours (Willson and Meyer, Ber. 1914, 47, 3162); *or*, in concentrated aqueous solution at 100°, added gradually to fused caustic soda in a covered vessel at about 300° (Wallach, *cf.* J. Soc. Chem. Ind. 1919, 38, 248).

Properties.—β-Naphthol crystallises in odourless scales or rhombic tables (*cf.* Groth, Annalen, 1869, 152, 285), m.p. 122° (Schäffer, *l.c.*), b.p. 285°–286° (Ebert and Merz, Ber. 1876, 9, 611), sp.gr. 1·217 at 4° (Schröder, Ber. 1879, 12, 1613), and is readily soluble in alcohol, organic solvents, or caustic alkali solutions, but only sparingly so in hot water. It sublimes easily and can be distilled with superheated steam, but is only slightly volatile with steam at 100°. It has marked antiseptic properties. The *sodium* compound $C_{10}H_7·ONa$ can be obtained crystalline (*v.* p. 466, footnote 1).

Reactions.—It couples readily with diazotised bases and is used extensively as end component for the production of *azo*-dyes either in the ordinary way or, if the dyestuff be insoluble, as a developer on the fibre. With nitrous acid it forms *nitroso-β-naphthol* (*v.* naphthaquinone-oximes) or, in ethereal solution, 1 : 6-*dinitro-β-naphthol*, which is also formed by nitration. Chlorination converts it into 1-*chloro-β-naphthol.* By sulphonation, *β-naphthol-mono-*, *di-* and *tri-sulphonic acids* are obtained.

On oxidation in alkaline solution with permanganate it yields either o-*carboxycinnamic acid* (Ehrlich and Benedikt, Monatsh. 1888, 9, 527) or *phthalonic acid* (Henriques, Ber. 1888, 21, 1618), but on fusion with caustic alkali and copper oxide or hydrated manganese peroxide, it is converted, like α-naphthol, into *phthalic acid* and *benzoic acid* (Bindsch., D. R.-P. 138790; 139956; Eng. P. 15527 of 1901). By reduction with sodium in boiling amyl alcohol solution it furnishes a mixture of ac.-*tetrahydro-β-naphthol* as chief product, with ar.-*tetrahydro-β-naphthol.* When heated with ammonium sulphite solution and ammonia at 100°–150°, or with ammonia under pressure, it is converted into *β-naphthylamine*, or with acetamide or aniline into *acetyl-* or *phenyl-β-naphthylamine*. By condensation with nitrosodimethylaniline hydrochloride it yields *Meldola's blue* (Meldola, Ber. 1879, 12, 2066).

Iodine solution added to a solution of β-naphthol in aqueous caustic soda (1 mol.) gives quantitatively a crystalline precipitate of 1-*iodo-β-naphthol*, m.p. 94° (Wilkie, J. Soc. Chem. Ind. 1911, 30, 402), but with excess of alkali a yellowish-green precipitate of so-called *β-naphthol iodide* (Messinger and Vortmann, Ber. 1889, 22, 2322; Bayer, D. R.-P. 49739; Eng. P. 5079 of 1889).

Colour reactions.—Bleaching-powder solution gives to an aqueous solution of β-naphthol a pale yellow colouration which disappears on addition of an excess. Ferric chloride, added to an aqueous solution, gives a pale green colouration, and afterwards a white flocculent precipitate of *ββ′-dinaphthol* (Dianin, Ber. 1873, 6, 1252; 1874, 7, 125; *cf.* Walder, Ber. 1882, 15, 2166). When warmed with strong caustic potash solution and chloroform at 50° it gives (like α-naphthol) a Prussian-blue colouration which gradually changes through green into brown (Lustgarten, Monatsh. 1882, 3, 720; *cf.* Rousseau, Ann. Chim. Phys. 1883, [v.] 28, 148).

Tests.—Commercial β-naphthol should be almost colourless, have approximately the right melting-point, and dissolve completely in caustic alkali forming an almost colourless solution.

Estimation.—A 1 p.c. solution of the sample in aqueous caustic soda (4 mols.) is titrated at 60° with excess of N/10 iodine (the equation is

$$C_{10}H_8O+3I_2+3NaOH=C_{10}H_5I_3O+3NaI+3H_2O)$$

cooled, acidified with dilute sulphuric acid, and the filtrate titrated back with N/10 sodium thiosulphate (Messinger and Vortmann, *l.c.*; *cf.* Kuster, Ber. 1894, 27, 1907; Wilkie, *l.c.*).

β-Naphthyl methyl ether (*nerolin*), prepared by heating β-naphthol (5 pts.) dissolved in absolute methyl alcohol (5 pts.) with sulphuric acid (2 pts.) in a reflux apparatus under slight pressure at 125° (Gattermann, Annalen, 1888, 244, 72), forms scales, m.p. 72°, b.p. 274° (Marchetti, Jahresb. Chem. 1879, 543), dissolves sparingly in alcohol, and has the odour of orange flowers (neroli).

β-Naphthyl ethyl ether, prepared like the methyl ether (Gattermann, *l.c.*; *cf.* Paul, Z. angew. Chem. 1896, 9, 620; Davis, Chem. Soc. Trans. 1900, 77, 33), m p. 37°, b.p. 282°, dissolves readily in alcohol, and has the odour of pineapple. On nitration it yields 1-*nitro-β-ethoxy-naphthalene*, m.p. 104° (Wittkampf, Ber. 1884, 17, 394; Cassella, D. P. Anm. C. 2883; Paul, *l.c.*); and, as minor product, 6-*nitro-β-ethoxy-naphthalene*, m.p. 114° (Gaess, J. pr. Chem. 1891, [ii.] 43, 22).

β-Naphthyl phenyl ether, m.p. 46°, is obtained when a solution of sodium β-naphtholate in β-naphthol is heated with chlorobenzene under pressure at 200°–220° (Fritzsche, D. R.-P. 269543; Eng. P. 9797 of 1913).

ββ′-Dinaphthyl ether $(C_{10}H_7)_2O$, obtained by boiling β-naphthol for some hours with 50 p.c. sulphuric acid (Graebe, Ber. 1880, 13, 1850); *or* by heating sodium 'β-naphthylsulphate'[1] *with β-naphthol at 180°–200°* (Nietzki, Ber. 1882, 15, 305); *or* β-naphthol *with* phosphorus pentachloride *(1 mol.)* at *100° for* 2 hours (Berger, Compt. rend. 1905, 141, 1027), forms scales, m.p. 105°, b.p. above 360°, and yields *β-naphthol-mono-*, *di-*, and *tri-sulphonic acids* when heated with sulphonating agents (Brönner, D. R.-P. 26938; Eng. P. 3606 of 1883).

ββ′-Dinaphthyl carbonate, which is obtained by the interaction of phosgene and sodium β-naphtholate (Schering, D. P. Anm. C. 4197), forms needles, m.p. 176°–177°, sparingly soluble in alcohol, and on sulphonation yields a mixture of the *β-naphthol*-6-, 7-, and 8-*sulphonic acids* (Reverdin and Kauffmann, Ber. 1895, 28, 3057).

ββ′-Dinaphthyl sulphite, a nacreous powder, is obtained by heating β-naphthol dissolved in carbon disulphide with thionyl chloride in presence of pyridine (Badische, D. R.-P. 303033).

β-Naphthyl acetate, obtained by heating β-naphthol with acetyl chloride (Schäffer, *l.c.*), or with acetic acid at 240° (Graebe, Annalen, 1881, 209, 150), forms needles, m.p. 70° (Miller, Ber. 1881, 14, 1602, footnote), dissolves sparingly in water, and is hydrolysed by distillation with steam.

β-Naphtholsulphonic Acids.

Introductory.—The greater number of the β-naphtholsulphonic acids is obtained by the sulphonation of β-naphthol, whereas in the α-series, for the production of α-naphtholsulphonic acids, direct sulphonation finds only a limited use. But this is only one of many differences between the two series. Another arises from (*a*) the preferential sulphonation in α- rather than in β- positions, (*b*) the preferential replacement of α- rather than of β-sulphonic groups by other radicles, which renders the methods most widely used in the α-series (*v.* p. 467) comparatively valueless for the production of β-naphtholsulphonic acids. For example:—

(i.) Fusion of naphthalenesulphonic acids with caustic alkali, if β-naphtholsulphonic acids are required, can be applied only to naphthalene-2:6- and 2:7-disulphonic acids, as these are the only two naphthalenepolysulphonic acids containing SO_3H radicles exclusively in β- positions.

(ii.) Exchange of the amino- group for hydroxyl in naphthylaminesulphonic acids, either by the diazo- reaction or by the bisulphite method, is limited in the β-series by the fact that the most convenient source of β-naphthylamine-sulphonic acids is found in the β-naphthol-sulphonic acids themselves.

The first product of the action of sulphuric acid on β-naphthol is β-naphthol-1-sulphonic acid, regarded by its discoverers as β-naphthylsulphuric acid. Without alteration in the concentration of the sulphuric acid, but with rise of temperature, there are obtained successively at 50°–60° β-naphthol-8-sulphonic acid, and at 90°–100° the 6-sulphonic acid. When the weight of sulphuric acid is doubled there are obtained, similarly, at 60° β-naphthol-6 : 8-disulphonic acid, and at 120°–130° the 3 : 6-disulphonic acid. With anhydro- acid, sulphonation of β-naphthol reaches its limit in the formation of the 3 : 6 : 8-trisulphonic acid. The relationship between these products is shown in the scheme[1]—

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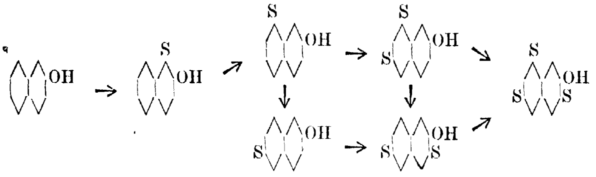
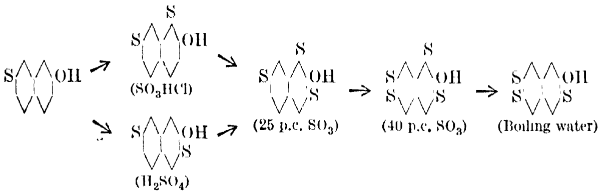
[1] The acid described by Armstrong (Ber. 1882, 15, 202) and by Nietzki (*l.c.*) as β-naphthylsulphuric acid is now known to be β-naphthol-1-sulphonic acid (*cf.* Tobias, D. R.-P. 74688).



Another source of β-naphtholpolysulphonic acids is the 7-sulphonic acid, which, although known to occur in the sulphonation product of β-naphthol at 100°–130°, does not seem to have been isolated from this source, but is obtained from naphthalene-2 : 7-disulphonic acid by fusion with caustic alkali. The acids formed from it by sulphonation are shown below, the sulphonating agent used being indicated under the symbol giving the constitution of the product.



Bearing in mind the rule of preferential substitution in α-positions, it is noteworthy that the SO_3H radicle is not found in either the 4- or the 5-position in any of the products of the sulphonation of β-naphthol under the most varied conditions. And with reference to the 1-position, it is evident that, of the five acids obtained from β-naphthol-7-sulphonic acid by sulphonation, the three containing a SO_3H radicle in this position are formed under conditions which exclude the presence of water; whereas the two from which it is absent are obtained respectively by the use of ordinary sulphuric acid, and by desulphonation with boiling water.

The β-naphtholsulphonates are better defined, and more easily separated from mixtures than are the α-naphtholsulphonates; they can therefore be employed for the production of pure β-naphthylaminesulphonic acids. Their chief use is in connexion with the manufacture of *ortho*-azo-dyes, but they are not equally valuable for this purpose. Thus, the 8-sulphonic and the 6 : 8-disulphonic acids, which, in comparison with the 6-sulphonic and 3 : 6-disulphonic acids, couple the more slowly with diazotised bases, furnish azo-dyes that are yellow or orange in shade rather than red and are the more highly prized. Hence, when first described, the 6 : 8-disulphonic acid was termed G-acid (Gelbsaure) and the 3 : 6-isomeride R-acid (Rotsaure) to recall this distinction (Hochst, D. R.-P. 3220).

β-NAPHTHOLMONOSULPHONIC ACIDS.[2]

(i.) β-**Naphthol-1-sulphonic acid** ('β-*naphthylsulphuric acid*'), obtained when a solution of β-naphthol in 2–2 5 times its weight of 90–92 p.c. sulphuric acid at 35°–45° is kept for a short time until it solidifies to a crystalline mass, is separated from the 8-sulphonic acid, also formed in small amount, either by salting out or by precipitation as the sparingly soluble

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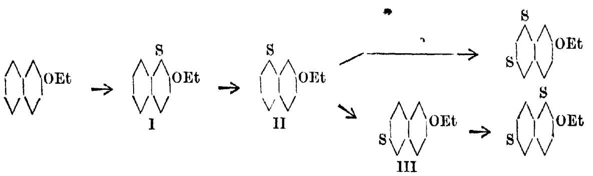
[1] This scheme is not to be regarded as complete. It leaves out of account the formation of β-naphthol-7-sulphonic acid (*q.v.*) recorded by Green, and should be compared with another, compiled from data furnished by Lapworth (Chem Soc Proc. 1895, 11, 49), in which the products formed in the sulphonation of β-ethoxynaphthalene by chlorosulphonic acid, under conditions excluding the presence of water, are displayed—



The change of acid I into acid II was found to take place at the ordinary temperature, and of acid II into acid III at the temperature of a water bath; moreover, acid III on sulphonation gave, not the 3 . 6-disulphonic acid as might be expected from the behaviour of β-naphthol-6-sulphonic acid, but the 1 : 6-disulphonic acid, not yet recognised among the sulphonation products of β-naphthol.

[2] In every case where the constitution of a β-naphtholsulphonic acid is given the OH radicle is supposed to be in the position '2.'

basic barium salt from the solution of the calcium salt obtained by neutralisation with lime (Tobias, D. R.-P. 74688; Eng. P. 15404 of 1893; *cf.* Nietzki, Ber. 1882, 15, 305). It is also formed when chlorosulphonic acid in mol. prop. is added to β-naphthol in carbon disulphide solution and the product, after removal of the solvent, heated at 100° (Armstrong, Ber. 1882, 15, 203).

Identification.—Both normal and basic salts are known, which with the exception of the *basic barium salt* are easily soluble in water. The normal *barium* salt $BaA_2+2C_2H_6O$, *potassium* salt KA, and *sodium* salt NaA, crystallise from alcohol in scales; the *disodium* salt, $Na_2A+2C_2H_6O$, in scales, shows no fluorescence in aqueous solution. In neutral solution the salts give an indigo-blue colouration with ferric chloride, and in acid solution decompose into β-naphthol and sulphuric acid on evaporation (Tobias, *l.c.*).

Reactions.—With diazotised bases coupling takes place in concentrated alkaline solution but owing to elimination of the SO_3H radicle the *azo*-dyes are derivatives of β-naphthol,[1] not of the sulphonic acid (Tobias, *l.c.*). In neutral or acid solution, by combination with diazotised *p*-nitraniline or dianisidine, *salts* are produced (Bayer, D. R.-P. 93305; Eng. P. 11757 of 1895). Dissolved in sulphuric acid it is converted at 50°–60° into *β-naphthol-6 : 8-disulphonic acid.* By the bisulphite reaction or when heated with 20 p.c. ammonia at 220°–230° it yields *β-naphthylamine-1-sulphonic acid.*

Its *acetyl* derivative, obtained by heating the sodium salt with acetic anhydride, is convertible into the *sulphonyl chloride*, m.p. 115·5°, which furnishes *β-naphthol-1-sulphonyl chloride*, needles, m.p. 124°, on de-acetylation (Anschutz and Maxim, Annalen, 1918, 415, 89).

(ii.) β-**Naphthol-4 sulphonic acid** is obtained from β-naphthylamine-4 : 8-disulphonic acid by digestion with water or 10 p.c. sulphuric acid under pressure at 170°–185° (Kalle, D. R.-P. 78603). Its *sodium* salt is easily soluble.

Reactions.—When heated with ammonia under pressure it is converted into *β-naphthylamine-4-sulphonic acid.* By digestion with 60 p.c. caustic soda solution at 230°–280° it yields *o-toluic acid* (Kalle, D. R.-P. 79028).

(iii.) β-**Naphthol-5-sulphonic acid** has been prepared from β-naphthylamine-5-sulphonic acid by the diazo-reaction (Dahl, D. R.-P. 29084; Eng. P. 7712 of 1884; Claus, J. pr. Chem. 1889, [ii.] 39, 315). The *azo*-dyes obtained from it are worthless (Dahl *l.c.*). On fusion with caustic alkali, it gives 1 : 6-*dihydroxynaphthalene.*

(iv.) β-**Naphthol-6-sulphonic acid** ([α-] *acid* of Armstrong and of Schultz; *Schäffer acid*) is formed as chief product, mixed with about 15–20 p.c. of the 8-sulphonic acid, when β-naphthol is heated on a water bath with twice its weight of sulphuric acid until completely sulphonated (Schaffer, Annalen, 1869, 152, 296); *or,* mixed with some 7-sulphonic acid, disulphonic acid and unattacked β-naphthol, when it is heated with monohydrate (1 mol) at 100°–105° for 2–3 hours (Armstrong, Ber. 1882, 15, 201; *cf.* Beyer and Kegel, D. R.-P. 32964; Eng. P. 7098 of 1884; Green, Chem. Soc. Trans. 1889, 55, 37); *or,* as chief product, when ββ′-dinaphthyl ether is sulphonated with 2–3 parts of sulphuric acid at 90°–100° (Brönner, D. R.-P. 26938; Eng. P. 3606 of 1883). The pure acid can be obtained from sodium naphthalene-2 : 6-disulphonate by fusing it with caustic alkali (Ebert and Merz, Ber. 1876, 9, 601; Armstrong and Graham, Chem. Soc. Trans. 1881, 39, 136; *cf.* Cassella, D. R.-P. 45221); *or* from 1-carboxy-β-naphthol-6-sulphonic acid by warming its aqueous solution at 60° (Seidler, D. R.-P. 53343); *or* from β-naphthylamine-6-sulphonic acid, either by the diazo-reaction, or by the bisulphite method (Badische, D. R.-P. 126136; 134401; *v.* p. 416).

Preparation.—β-Naphthol (1 mol.) in fine powder is stirred with monohydrate (2 mols.) at 100° until sulphonation is complete. The product is then diluted with water, the mixed acids converted into sodium salts after neutralisation with lime and the filtrate, after concentration to about 5 times the volume of monohydrate used, stirred with sufficient common salt for it to contain 20 p.c. NaCl, whereby the less soluble sodium β-naphthol-6-sulphonate is separated completely from the more soluble salts of the accompanying acids, chiefly β-naphthol-3 : 6-disulphonic or R-acid. The mother liquor can be worked up for R-acid (*q.v.*), which may amount to one-half of the Schaffer acid obtained[2] (Fierz-David, Dye Chemistry, p. 33). If the sulphonation be conducted at a lower temperature or with a smaller proportion of acid (1 mol.), the same mode of separation is followed but β-naphthol-8-sulphonate will remain in the mother liquor.

Identification.—The *acid* forms easily soluble, non-deliquescent scales, m.p. 125°; the *lead* salt PbA_2+6H_2O, scales; the *barium* salt BaA_2+6H_2O, long prisms; the *calcium* salt CaA_2+5H_2O, scales, readily soluble in alcohol or in 30 parts of water at 18°; the *potassium* salt KA, prisms, soluble in about 50 parts of water at 15°; the *sodium* salt $NaA+2H_2O$, scales, soluble in about 3·3 parts of water at 80°, in 57·8 parts at 14°, and in 69 parts at 11·5° (Schaffer, *l.c.*; Armstrong and Graham, *l.c.*); the *ammonium* salt NH_4A, long flat prisms soluble in about 34 parts of water at 24° (Meldola, Chem. Soc. Trans. 1881, 39, 41). In aqueous solution the salts show a pale blue fluorescence and give a pale green colouration with ferric chloride. With nitric acid, solutions of these salts become carmine-red when warmed (Schafter, *l.c.*; Armstrong and Graham, *l.c.*) owing to the formation of an *indophenol* derivative of [β-]naphthaquinone, which can be isolated in red crystals (Nietzki and Knapp, Ber. 1897, 30, 87).

Reactions.—It couples with diazotised bases forming *azo-* dyes. With nitrous acid it forms 1-*nitroso-β-naphthol-6-sulphonic acid* convertible into a *naphthol green* by ferric chloride. On sulphonation with anhydro-acid at 160°, it yields *β-naphthol-3 : 6-disulphonic acid.* By the bisulphite reaction or when heated with ammonia under pressure, it is converted into

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[1] The magnesium salt is employed in place of β-naphthol as a developer of dyestuffs on the fibre (Calico.Printers' Association and Fourneaux, D. R.-P. 204702).

[2] Methods for determining the relative proportion of Schäffer and R-acids in a mixture are given by Fierz-David (*l.c.*).

β-naphthylamine-6-sulphonic acid. Fusion with caustic alkali furnishes 2 : 6-*dihydroxynaphthalene.* With sulphur and caustic alkali solution under pressure at 200° it gives two 'thio-β-naphtholsulphonic acids' (Aktienges., D. R.-P. 50077).

Derivatives.—The phenyl ester, needles, m.p. 131°; amide, scales, m.p. 237°–239°; dimethylamide, scales, m.p. 125°; and anilide, needles, m.p. 161°, have been obtained from the corresponding derivatives of 1-carboxy-β-naphthol-6-sulphonyl chloride by elimination of carbon dioxide (Bayer, D. R.-P. 278091). They couple with diazotised bases forming *azo*-dyes.

(v.) β-**Naphthol**-7-**sulphonic acid** ([δ-] *acid*; F- *acid*) is obtained technically from sodium naphthalene-2 : 7-disulphonate by digestion with 50–90 p.c. caustic soda solution at 250° (Weinberg, Ber. 1887, 20, 2907; Cassella, D. R.-P. 42112; Eng. P. 12908 of 1886). Mixed with the 6-sulphonic acid it is formed when β-naphthol is heated with monohydrate (1 mol.) at 100°–130° for 2–3 hours, but does not seem to have been isolated from the product (Green, Eng. P. 15849 of 1888; Chem. Soc. Trans. 1889, 55, 37). From β-naphthylamine-7-sulphonic acid it can be obtained either by the diazo- reaction (Bayer and Duisberg, Ber. 1887, 20, 1431; *cf.* Schultz, *ibid.* 3158) or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 69, 73; *v.* p. 416).

Preparation.—Sodium naphthalene-2 : 7-disulphonate is digested with four times its weight of 50 p.c. caustic soda solution under pressure at 225° for 10 hours or until an acidified test gives traces of dihydroxynaphthalene when extracted by ether, or a test freed from sulphur dioxide gives with diazoxylene an amount of azo-dye equivalent to the quantity of sodium salt employed. From the solution of the melt in twice its weight of water, after it has been acidified and boiled to remove sulphur dioxide, sodium β-naphthol-7-sulphonate crystallises in the cold (Cassella, *l.c.*). Alternatively, the crude mixture of sodium naphthalene-2 : 6- and 2 : 7-disulphonate may be used, and the isomeric β-naphtholsulphonic acids separated by taking advantage of the sparing solubility either of the basic sodium 6-sulphonate in the cold alkaline liquor saturated with common salt or of the normal sodium 6-sulphonate in a boiling solution of the melt in 2–3 vols. of water acidified by hydrochloric acid and saturated with common salt (Cassella, D. R.-P. 45221).

Identification.—The *acid* forms hydrated needles, m.p. 89°, readily soluble in water or alcohol; the *barium* salt sparingly soluble prisms; the *magnesium* salt $MgA_2+5\frac{1}{2}H_2O$, scales; the *potassium* salt $KA+H_2O$, readily soluble rhombs; the *sodium*[1] salt $NaA+2\frac{1}{2}H_2O$, large scales soluble in 12·5 parts of water at 15° (Weinberg, *l.c.*). In alkaline solution the salts show a pure blue fluorescence, and in neutral solution give a dark blue colouration with ferric chloride (Cassella, *l.c.*).

Reactions.—It couples with diazotised bases forming *azo*-dyes. With nitrous acid it gives 1-*nitroso-β-naphthol*-7-*sulphonic acid*, convertible into a *naphthol green* by iron salts (Cassella, D. R.-P. 42112; Eng. P. 12908 of 1886). On sulphonation with chlorosulphonic acid it yields *β-naphthol*-1 : 7-*disulphonic acid*, but with sulphuric acid at 120° the 3 : 7-*disulphonic acid.* By the bisulphite method or when heated with 20 p.c. ammonia at 250°, it is converted into *β-naphthylamine-7-sulphonic acid*; with dimethylamine at 220° the product is *dimethyl-β-naphthylamine-7-sulphonic acid.* Fused with caustic alkali, it furnishes 2 : 7-*dihydroxynaphthalene.*

(vi.) β-**Naphthol**-8-**sulphonic acid** ([α-] *acid* of Bayer's patents; [β-] *acid* of Schultz; and o-*acid* of Claus and Volz;[2] *croceic acid*; *Bayer* or *Rumpff acid*) is formed as chief product (80 p.c.) together with the 2 : 6-disulphonic acid when finely powdered β-naphthol is stirred as rapidly as possible into twice its weight of sulphuric acid either at 50° or 60° until, in the course of 15 minutes, it is dissolved (Bayer, D. R.-P. 18027; 20397; 26231[3]; Eng. P. 1225 of 1881; 2411 of 1883) or during several days at a temperature not exceeding 20°, the 1-sulphonic acid first formed being converted mainly into the 8-sulphonic, mixed only with a small amount of the 6-sulphonic acid (Leonhardt and Schulz, D. R.-P. 33857; *cf.* Bang and Roussin, D. P. Anm. B. 13709). It occurs (15–20 p.c.) in the product formed when β-naphthol is heated with twice its weight of sulphuric acid on a water-bath until dissolved (Schaffer, Annalen, 1869, 152, 296), and in the so-called Armstrong acid produced when β-naphthol is heated with monohydrate (1 mol.) at 100° (Beyer and Kegel, D. R.-P. 32964; Eng. P. 7098 of 1884).

From β-naphthylamine-8-sulphonic acid it is obtained pure, either by the bisulphite reaction (Badische, D. R.-P. 134401; *v.* p. 416) or by boiling its diazo- compound with 2 p.c. sulphuric acid (Dahl, D. R.-P. 29084; Eng. P. 7712 of 1884).

Preparation.—When obtained from β-naphthol by either Bayer's or Leonhardt's process it can be freed from the accompanying 6-isomeride by converting the sulphonation product into calcium salt, filtering the solution while hot, and concentrating the filtrate until the 6-sulphonate separates out as a precipitate. About four-fifths of the 6-sulphonic acid being removed as calcium salt, the remainder can be separated from the mother liquor by conversion into neutral (basic) sodium salt, which is either coupled with the requisite quantity of a diazotised base (as determined by a preliminary test) and the dye salted out, or, less advantageously, dried and extracted with 90 p.c. alcohol in which sodium β-naphthol-6-sulphonate is practically insoluble. The filtrate in either case contains the sodium β-naphthol-8-sulphonate (*cf.* Bayer, *l.c.*; D. R.-P. 30077; Eng P. 8495 of 1884).

Identification.—The *acid* decomposes into β-naphthol and sulphuric acid when its solution is evaporated; it forms both normal (acid) and basic (neutral) salts, which are much more soluble in water than the salts of the 6-sulphonic acid. The *barium* and *calcium* salts are insoluble in absolute alcohol; the *lead* salt $PbA_2+2\frac{1}{2}H_2O$, forms rhombohedra; the *zinc* salt ZnA_2+2H_2O, needles; the *sodium* salt NaA, six-sided scales; the basic *disodium* salt $Na_2A+2C_2H_6O$, deliquescent needles from 95 p.c. alcohol in which it dissolves very easily at the boiling-point, but only sparingly (1 in 100) at 15° (Badische, D. R.-P. 20760; Claus and Volz, Ber. 1885, 18, 3155). Unlike its isomerides, it does not give a nitroso-compound (Gans & Co., D. R.-P. 28065; Eng. P. 2269 of 1884).

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[1] The sodium salt under the name 'shading salt' (Nuanciersalz) is used for shading, *e.g.* in Para-red dyeing.

[2] Claus and Volz assign the constitution [2 : 3] to this acid, but the method employed by them has been shown to be untrustworthy (*cf.* Armstrong, Chem. Soc. Proc. 1889, 5, 9; Pfitzinger and Duisberg, Ber. 1889, 22, 397; Nietzki and Zübelen, *ibid.* 454).

[3] In this Patent reference is made to the presence of a third acid in the sulphonation product, but although regarded as a β-naphthol derivative (Bayer, D. R.-P. 80077; Eng. P. 8495 of 1884) it does not appear to have been identified or characterised.

Reactions.—It couples with diazotised bases, but only very slowly, forming valuable *azo*-dyes. When warmed with dilute nitric acid it yields 1 : 6-*dinitro-β-naphthol*-8-*sulphonic acid* (crocein yellow). On sulphonation with sulphuric acid below 50°, it gives *β-naphthol*-6 : 8-*disulphonic acid.* By the bisulphite reaction or when heated with ammonia under pressure it is converted into *β-naphthylamine*-8-*sulphonic acid.* Fused with caustic alkali, it furnishes 1 : 7-*dihydroxynaphthalene.*

β-NAPHTHOLDISULPHONIC ACIDS.

(i.) β-**Naphthol**-1 : 6-**disulphonic acid** is mentioned by Bucherer (J. pr. Chem. 1904, [ii.] 69, 73; *cf.* Badische, D. R.-P. 117471; Eng. P. 1387 of 1900) as furnishing the corresponding naphthylamine derivative by the bisulphite method, but no description of it seems to have been published.

The ethyl ether has been obtained by sulphonating β-ethoxynaphthalene or its 6-sulphonyl chloride in chloroform solution with chlorosulphonic acid (Lapworth, Chem. Soc. Proc. 1895, 11, 51).

(ii.) β-**Naphthol**-1 : 7-**disulphonic acid** is obtained either from sodium β-naphthol-7-sulphonate by sulphonation in the cold with chlorosulphonic acid (Bayer, D. R.-P. 77596; Eng. P. 1063 of 1894; Dressel and Kothe, Ber. 1894, 27, 1206), or from β-naphthylamine-1 : 7-disulphonic acid by the diazo-reaction Dressel and Kothe, *ibid.* 1207).

Identification.—The *barium* salt forms sparingly soluble needles; the *potassium* salt $K_2A+1\frac{1}{2}H_2O$, moderately soluble prisms; the *sodium* salt, very soluble needles. In alkaline solution the salts give a pale blue fluorescence. It does not couple with diazotised bases.

Reactions.—When boiled with 10 p.c. hydrochloric acid, it reverts to *β-naphthol*-7-*sulphonic acid.* By digestion with 25 p.c. ammonia solution at 180°–200°, or by the bisulphite reaction it is converted into *β-naphthylamine*-1 : 7-*disulphonic acid.*

(iii.) β-**Naphthol**-3 : 6-**disulphonic acid** (*β-naphthol*-[*a*-]*disulphonic acid*; R-*acid*) is formed as chief product, mixed with some 6 : 8-disulphonic acid, when β-naphthol is heated with 3–4 times its weight of sulphuric acid at 100°–110° for 12 hours (Höchst, D. R.-P. 3229; Eng. P. 1715 of 1878; Griess, Ber. 1880, 13, 1956), or at 125°–150° for 5–6 hours (Beyer and Kegel, D. R.-P. 33916; Eng. P. 7097 of 1884). It is said to be the only product when equal weights of potassium β-naphthol-6-sulphonate, potassium pyrosulphate, and sulphuric acid are heated together for 5–6 hours at 160° (Baum. D. P. Anm. B. 4199; Eng. P. 3523 (prov. spec.) of 1883).

Preparation.—Finely powdered β-naphthol is stirred into 4 times its weight of sulphuric acid without cooling and the product heated at 120° with continuous stirring until a sample, on the addition of sodium nitrite in excess, no longer gives the red colouration characteristic of β-naphthol-6-sulphonic acid. It is then converted through the calcium into the sodium salt which from a concentrated solution is precipitated as acid sodium salt by saturation with common salt, or in the dry state is extracted by alcohol to remove 6 : 8-disulphonate or other impurities, R-salt being practically insoluble in this solvent (*cf.* Höchst, *l.c.*). Alternatively, the greater part of the R-acid in the product may be separated as the crystalline sodium salt by pouring the sulphonation melt into brine, the mother liquor retaining the 6 : 8-salt with the remainder of the R-salt (Beyer and Kegel, *l.c.*).

Identification.—The *acid* forms silky, deliquescent needles, very soluble in water or alcohol; the *barium* salt $BaA+6H_2O$, needles soluble in 12 parts of boiling water, but insoluble in alcohol; the *sodium* salt, aggregates of minute needles readily soluble in cold water, but only sparingly so in alcohol or in brine. In aqueous solution the salts show a bluish-green fluorescence (Griess, *l.c.*). The readily soluble *aluminium* salt has been introduced as an antiseptic and astringent under the name 'Alumnol' (Hochst, D. R.-P. 74209; Eng. P. 10668 of 1892).

Reactions.—It couples readily with diazotised bases and is an important component of *azo*-dyes. With nitrous acid the 1-*nitroso*-derivative is formed. By sulphonation with 20 p.c. anhydro-acid, it is converted into *β-naphthol*-3 : 6 : 8-*trisulphonic acid.* Heated with dilute (20 p.c.) mineral acids it is not hydrolysed at the boiling-point (*cf.* Bayer, D. R.-P. 77596), although at higher temperatures or by means of sodium amalgam in the cold, it reverts to *β-naphthol*-6-*sulphonic acid* (Friedländer and Lucht, Ber. 1893, 26, 3029). By the bisulphite reaction or when heated with ammonia under pressure, it yields *β-naphthylamine*-3 : 6-*disulphonic acid.* Fused with caustic soda at 220°–240°, it gives 2 : 3-*dihydroxynaphthalene*-6-*sulphonic acid.*

(iv.) β-**Naphthol**-3 : 7-**disulphonic acid** (*β-naphthol*-[δ-]*disulphonic acid*; F-*acid*), formed when sodium β-naphthol-7-sulphonate is heated either with twice its weight of sulphuric acid at 120° for about 12 hours (Cassella, D. R.-P. 44079; Eng. P. 8265 of 1887), or with 3–4 times its weight of the acid on a water-bath (Dressel and Kothe, Ber. 1894, 27, 1206), can also be obtained by partial hydrolysis of β-naphthol-1 : 3 : 7-trisulphonic acid with 10 p.c. hydrochloric acid (Bayer, D. R.-P. 78569, Eng. P. 17141 of 1893; Dressel and Kothe, *l.c.*).

Identification.—The *barium* salt $BaA+2\frac{1}{2}H_2O$, forms small prisms soluble in 185 parts of boiling water; the *sodium* salt Na_2A is soluble in 100 parts of 80 p.c. alcohol and very soluble in water, the solution showing green fluorescence (Cassella, *l.c.*; Weinberg, Ber. 1887, 20, 2911).

Reactions.—It couples with diazotised bases forming *azo*-dyes. By sulphonation with 25 p.c.

anhydro- acid at 80°–90° it is converted into *β-naphthol*-1 : 3 : 7-*trisulphonic acid.* Heated with dilute (20 p.c.) mineral acids it is not hydrolysed at the boiling-point (*cf.* Bayer, D. R.-P. 77596; Eng. P. 1063 of 1894), but at higher temperatures regenerates *β-naphthol*-7-*sulphonic acid.* By the bisulphite reaction or when heated with 25 p.c. ammonia solution at 200° it yields *β-naphthylamine*-3 : 7-*disulphonic acid.* Fused with caustic alkali it gives 2 : 7-*dihydroxynaphthalene*-3-*sulphonic acid.*

(v.) **β-Naphthol-4 : 7-disulphonic acid** has been prepared by boiling diazotised β-naphthylamine-4 : 7-disulphonic acid with water, but its salts have not been described. When heated with aniline and aniline hydrochloride at 150°–170° it is converted into *diphenyl*-1 : 3-*diaminonaphthalene*-6-*sulphonic acid* (Bayer, D. R.-P. 77866; Eng. P. 16780 of 1893).

(vi.) **β-Naphthol-4 : 8-disulphonic acid** (*C-acid*) is obtained from β-naphthylamine-4 : 8-disulphonic acid by the diazo-reaction. The *calcium* salt forms prisms; the solution of the *sodium* salt shows blue fluorescence (Cassella, D. R.-P. 65997).

Reactions—In concentrated solution it couples with diazotised bases forming *azo*-dyes. On desulphonation by means of zinc-dust and boiling dilute caustic soda solution, it yields both *β-naphthol*-4- and 8-*sulphonic acids* (Kalle, D. R.-P. 233934). Digestion with aniline and aniline hydrochloride at 150°–170° converts it into *diphenyl*-1 : 3-*diaminonaphthalene*-5-*sulphonic acid.*

(vii.) **β-Naphthol-5 : 7-disulphonic acid** has been prepared from β-naphthylamine-5 : 7-disulphonic acid by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 70, 347; Badische, D. R.-P. 134401; *v.* p. 416). No description of the acid has been published.

(viii.) **β-Naphthol-6 : 8-disulphonic acid** (*β-naphthol*-[*γ*-]*disulphonic acid*; *G-acid*; *Y-acid* of some English patents; also known as *β-naphthol*-[*β*-]*disulphonic acid* when mixed with some R-acid, *cf.* Griess, Ber. 1880, 13, 1956), is formed as chief product when a mixture of β-naphthol either with 5 parts of sulphuric acid at 0° is gradually heated to 60° in the course of 36 hours, or with 4 parts of acid is maintained at 60° during 48 hours or at 20° during 8–10 days (Hochst, D. R.-P. 36491; Gans and Hoffmann, Eng. P. 816 of 1884); *or* when β-naphthol-8-sulphonic acid, mixed with 3 times its weight of sulphuric acid, is either heated at 40°–50° during 5–6 hours or left at 25° for 8–10 days (Gans and Hoffmann, *l.c.*). It has been prepared from β-naphthylamine-6 : 8-disulphonic acid by the diazo-reaction (Gans & Co., D. R.-P. 35019; Eng. P. 816 of 1884).

Preparation.—Finely powdered β-naphthol is added slowly to 3 times its weight of monohydrate, the temperature being kept below 35° by cooling and the mixture stirred continuously at this temperature during many hours until a test with a small quantity of water no longer gives a precipitate of β-naphthol. Poured into a relatively small volume of water, the product is converted through the calcium into the potassium salt and the filtrate after concentration to a small bulk then rendered acid by hydrochloric acid added in excess to achieve separation of the G- constituent as acid potassium salt from the more soluble R-salt which can be salted out from the filtrate. The weight of R-salt isolated is about equal to that of the β-naphthol sulphonated, while that of the G-salt is about 10 p.c. more (*cf.* Fierz-David, Dye Chemistry, p. 34). Or the sulphonation product may be purified by taking advantage of the fact that G-acid, like the 8-monosulphonic acid, couples less readily with diazo- compounds than the accompanying Schäffer and R-acids. The process consists in adding to an alkaline solution of the sodium salt the quantity of diazo-compound calculated from a test, and salting out the azo-dye; the filtrate contains the sodium salt of technically pure G-acid (Höchst, *l.c.*).

Identification.—With the exception of the *potassium* salt which dissolves in 2·5 parts of boiling water, the salts of pure G-acid are much more soluble in water than the corresponding R- or Schaffer salts, the first (incomplete) separation of G- from R-acid being achieved by fractional crystallisation of the mixed barium salts (Griess, *l.c.*).

Reactions.—It couples only slowly and in concentrated solutions with diazotised bases, but is an important source of *azo-* dyes. By sulphonation with 20 p.c. anhydro- acid it is converted into *β-naphthol*-3 : 6 : 8-*trisulphonic acid.* Heated with dilute (20 p.c.) mineral acids, it is not hydrolysed at the boiling-point (*cf.* Bayer, D. R.-P. 77596), but at higher temperatures or by means of sodium amalgam in the cold furnishes *β-naphthol*-6-*sulphonic acid* (Friedlander and Lucht, Ber. 1893, 26, 3032). By the bisulphite method or when heated with ammonia under pressure, it yields *β-naphthylamine*-6 : 8-*disulphonic acid.* Fused with caustic soda at 200°–230° it gives 1 : 7-*dihydroxynaphthalene*-3-*sulphonic acid,* but at 260°–320° *hydroxytoluic acid* (Hochst, D. R.-P. 81333).

β-NAPHTHOLTRISULPHONIC ACIDS.

(i.) **β-Naphthol-1 : 3 : 7-trisulphonic acid** is prepared by sulphonating either β-naphthol-7-sulphonic acid or β-naphthol-3 : 7-disulphonic acid with 25 p.c. anhydro- acid at 80°–90° (Bayer, D. R.-P. 78569; Eng. P. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1207).

Identification.—The *barium* salt is easily soluble; the *sodium* salt Na_3A is very soluble in water, but only sparingly so in alcohol, gives with ferric chloride a violet colouration and in alkaline solution shows a bluish-green fluorescence. It does not couple with diazotised bases (Dressel and Kothe, *l.c.*).

Reactions.—By sulphonation with 40 p.c. anhydro-acid at 120°–130° it is converted into *β-naphthol*-1 : 3 : 6 : 7-*tetrasulphonic acid*; when boiled with dilute (10 p.c.) mineral acids, it reverts to *β-naphthol*-3 : 7-*disulphonic acid.* Digestion with 25 p.c. ammonia at 190° converts it into *β-naphthylamine*-1 : 3 : 7-*trisulphonic acid.*

(ii.) **β-Naphthol-3 : 5 : 7-trisulphonic acid,** obtained from β-naphthylamine-3 : 5 : 7-trisulphonic acid by the diazo-reaction, couples with diazotised bases forming *azo-* dyes (Dressel and Kothe, Ber. 1894, 27, 1203).

(iii.) **β-Naphthol-3 : 6 : 7-trisulphonic acid** is formed either from β-naphthol-1 : 3 : 6 : 7-tetrasulphonic acid by boiling it with water or dilute acids (Bayer, D. R.-P. 78569; Eng. P. 17141 of

1893; Dressel and Kothe, Ber. 1894, 27, 1209), or from β-naphthylamine-3 : 6 : 7-trisulphonic acid by the diazo- reaction (Dressel and Kothe, *l.c.*).

Identification.—The *barium* salt is gelatinous; the *sodium* salt Na_3A, in needles, is less soluble than its isomerides in water, brine or alcohol, gives a violet colouration with ferric chloride, and shows in alkaline solution a bluish-green fluorescence.

Reactions.—It couples in alkaline solution with diazotised bases forming *azo-* dyes, but in neutral or acid solution combines with tetrazo-derivatives of the diphenyl series forming *salts* (Bayer, D. R.-P. 92169; Eng. P. 8995 of 1895). When heated with 25 p.c. ammonia solution it yields *β-naphthylamine*-3 : 6 : 7-*trisulphonic acid.* It is not hydrolysed by dilute acids. Digestion with 66 p.c. caustic soda solution at 220°–300° converts it into 2 : 7-*dihydroxynaphthalene*-3 : 6-*disulphonic acid.*

(iv.) β-**Naphthol**-3 : 6 : 8-**trisulphonic acid** has been prepared by stirring β-naphthol with 4–5 times its weight of 20 p.c. anhydro- acid at 140°–160° until a test gives with ammonia a solution showing a pure green fluorescence, or in alkaline solution with diazotised xylidine furnishes an azo- dye only after some time (Meldola, Eng. P. 1864 of 1879; Höchst, D R.-P. 22038; Eng. P. 2544 of 1882); *or* by heating it with 40 p.c. anhydro- acid at 90°–120° (Nietzki, Chem. Zeit. 1891, 15, 296); *or* by stirring it into 3 times its weight of monohydrate, and, after adding an equal weight of 40 p.c. anhydro- acid, heating the mixture at 125° for 2 hours, then adding brine to separate out the acid sodium salt (Levinstein, Eng. P. 706 of 1883). Or β-naphthol may be replaced by β-naphthol-6- or 8-monosulphonic acid, *or* β-naphthol-3 : 6- or 6 : 8-disulphonic acid (*cf.* Levinstein, *l.c.*; Ber 1883, 16, 462; Limpach, *ibid.* 726).

By Nietzki's process a crystalline powder is obtained when the melt is mixed with 3 times its weight of ice. This is considered to be a 2 : 3-anhydride or sultone. In solution it is non-fluorescent, and does not give a colouration with ferric chloride. Alkalis convert it into salts of the trisulphonic acid, which with ferric chloride give a violet colouration, and in alkaline solution show a yellowish-green fluorescence (Nietzki, *l.c.*).

Reactions.—It couples with diazotised bases forming *azo-* dyes. Desulphonated by sodium amalgam in the cold it reverts to *β-naphthol*-3 : 6-*disulphonic acid* (Bayer, D. R.-P. 255724; Eng. P. 28172 of 1911) When heated with ammonia at 200°–250° it yields *β-naphthylamine*-3 : 6 : 8-*trisulphonic acid.* By fusion with caustic alkali at 220°–230° it gives a mixture of 1 : 7-*dihydroxynaphthalene*-3 : 6-*disulphonic* and 2 : 3-*dihydroxynaphthalene*-6 : 8-*disulphonic acids.*

β-NAPHTHOLTETRASULPHONIC ACID.

β-**Naphthol**-1 : 3 : 6 : 7-**tetrasulphonic acid** is obtained by the sulphonation of β-naphthol-7-sulphonic, or 3 : 7-disulphonic, or 1 : 3 : 7-trisulphonic acid with 40 p.c. anhydro- acid at 120°–130°, but undergoes desulphonation unless care be taken to prevent the solution of the melt in water, so long as it is acid, becoming warm (Bayer, D. P. Anm. F. 6991; Eng. P. 17141 of 1893; Dressel and Kothe, Ber. 1894, 27, 1203).

Identification.—The *barium* salt is a very sparingly soluble sandy powder; the *sodium* salt Na_4A is easily soluble in water but insoluble in alcohol, and in alkaline solution shows a bluish-green fluorescence. It does not couple with diazotised bases.

Reactions.—Digestion with 25 p.c. ammonia solution at 180° converts it into *β-naphthylamine*-1 : 3 : 6 : 7-*tetrasulphonic acid.* When boiled with dilute mineral acids it yields *β-naphthol*-2 : 6 : 7-*trisulphonic acid.*

CHLORO-β-NAPHTHOL.

Introductory.—When chlorinated, β-naphthol furnishes 1-*chloro-β-naphthol*, followed by the additive compounds, *dichloro-β-keto-* and *tetrachloro-β-ketonaphthalene* (Zincke and Kegel, Ber. 1888, 21, 3378).

1-**Chloro**-β-**naphthol**, obtained by chlorinating β-naphthol in acetic acid solution (Cleve, Ber. 1888, 21, 895), or, better, by the action of hypochlorous acid in mol. prop. on β-naphthol dissolved in alkali (Kalle, D. R.-P. 168824), forms monoclinic crystals, m.p. 70°–71°.

NITROSO-β-NAPHTHOLS.

(*v. Naphthaquinoneoximes.*)

NITRO-β-NAPHTHOLS.

(i.) 1-**Nitro**-β-**naphthol** is produced when 1-nitroso-β-naphthol is oxidised by dilute nitric acid (Stenhouse and Groves, Chem. Soc. Trans. 1877, 32, 51; *cf.* Hewitt and Mitchell, *ibid.* 1906, 89, 1172); *or* when acetyl-1-nitro-β-naphthylamine is boiled with 6 p.c. caustic soda solution (Liebermann and Jacobson, Annalen, 1882, 211, 46); *or* when α-nitronaphthalene is heated at 50°–60° with 20 times its weight of pulverised caustic soda (Wohl, D. R.-P. 116790; *cf.* Wohl and Aue, Ber. 1901, 34, 2444). It forms yellow needles, m.p. 103°; its *sodium* salt, red needles; *ethyl ether*, yellow needles, m.p. 103°–104° (Wittkampf, Ber. 1884, 17, 394), and *acetate*, colourless needles, m.p. 61° (Böttcher, Ber. 1883, 16, 1938).

(ii.) 4-**Nitro**-β-**naphthol**, obtained from 2 : 4-dinitro-α-naphthylamine by heating the derived 1-diazo-2-oxide with powdered aluminium and alcohol, forms yellow needles, m.p. 120°, is much less easily alkylated than β-naphthol and couples more slowly with diazotised bases (Morgan and Evens, Chem. Soc. Trans. 1919, 115, 1132; Morgan and Brit. Dyestuffs Corp., Brit. P. 152437).

(iii.) 5-**Nitro**-β-**naphthol**, prepared from 5-nitro-β-naphthylamine by the diazo- reaction, crystallises from water in yellow needles, m.p. 147°. The salts are reddish-yellow and easily soluble; the *ethyl ether* forms yellow needles, m.p. 115° (Friedländer and Szymanski, Ber. 1892, 25, 2079).

(iv.) 8-**Nitro**-β-**naphthol**, obtained from the ethyl ether by hydrolysis with hydrochloric acid at 160° (Gaess, J. pr. Chem. 1891, [ii.] 44, 614), *or* from 8-nitro-β-naphthylamine by the diazo- reaction (Friedländer and Szymanski, Ber. 1892, 25, 2082), forms deep yellow needles, m.p. 144°–145°. The *ethyl ether*, prepared by nitration of β-ethoxynaphthalene, forms long golden-yellow needles, m.p. 72°–73° (Gaess, J. pr. Chem. 1891, [ii.] 43, 25), and the *acetate*, needles, m.p. 101°–102° (Gaess, *ibid.* 1892, [ii.] 45, 615).

DINITRO-β-NAPHTHOL.

1 : 6-**Dinitro-β-naphthol** is formed from β-naphthol by nitration in alcoholic solution (Wallach and Wichelhaus, Ber. 1870, 3, 846), or by means of nitrous fumes in cold ethereal solution (Schmidt, Ber. 1900, 33, 3246); *or* by boiling diazotised β-naphthylamine with dilute nitric acid (Graebe and Drews, Ber. 1884, 17, 1170), *or* by allowing a solution of 1-nitro-1-bromo-2-ketodihydronaphthalene in acetic acid to remain in the cold for some days (Fries, Annalen, 1912, 389, 317).

Properties.—It crystallises in yellow needles, m.p. 195°; the *potassium* salt $KA+2H_2O$, in sparingly soluble needles; and the *ethyl ether*, in yellow needles, m.p. 144° (Gaess, J. pr. Chem. 1891, [ii.] 43, 29). It dyes wool and silk yellow. When heated with alcoholic ammonia at 150°–160°, it yields 1 : 6-*dinitro-β-naphthylamine* (Kehrmann and Matis, Ber. 1898, 31, 2419).

The 8-sulphonic acid (*crocein yellow*) is produced by warming sodium β-naphthol-8-sulphonate with dilute nitric acid at 30°–40° until nitration is complete (Bayer, D. R.-P. 18027; Eng. P. 1225 of 1881; Nietzki and Zubelen, Ber. 1889, 22, 454). The *potassium* salt KA forms yellow needles, and the *basic potassium* salt K_2A, sparingly soluble, yellow scales. It dyes wool yellow, but has little tinctorial power.

VII. AMINOHYDROXY- DERIVATIVES.

Introductory.—All the fourteen isomeric aminonaphthols, the existence of which is deducible from the naphthalene formula, have been prepared and are obtained by methods that usually afford evidence of their structure. Summarised, these methods are—

(1) Reduction of the corresponding nitronaphthols;

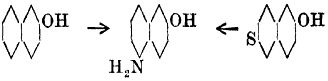
(2) Reduction of nitroso- or azo- derivatives of α- or β-naphthol;

(3) Fusion of α- or β-naphthylaminemonosulphonic acids with caustic alkali, α-naphthylamine-4-sulphonic acid being an exception, as it furnishes α-naphthol-4-sulphonic acid under these conditions;

(4) Fusion of naphtholmonosulphonic acids with sodamide;

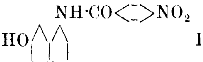
(5) Interaction of dihydroxynaphthalenes with ammonia, or with ammonium bisulphite and ammonia.

The sodamide reaction, although the only method for the direct conversion of naphtholmonosulphonic acids into aminonaphthols, furnishes but two examples of this replacement of the SO_3H by the NH_2 radicle—*viz.* the conversion of α-naphthol-5- and 8-sulphonic acid into 5-amino- and 8-amino-α-naphthol respectively. From the two naphthols, 5-amino-α- and 5-amino-β-naphthol are obtained, and 5-amino-β-naphthol is also the product when β-naphthol-6-, 7-,[1] or 8 sulphonic acid is fused with sodamide owing to β-naphthol being formed at an intermediate stage in the reaction (Sachs, Ber. 1906, 39, 3010).



The aminonaphthols are basic compounds forming salts with acids; but, nevertheless, dissolve readily in alkalis. In solution, or in the moist state, they are readily oxidised in the air, and those which contain the radicles relatively in 1 : 2- or 1 : 4- positions form naphthaquinones on oxidation with ferric chloride, chromic acid, or nitrous acid in acid solution.

By condensation with certain acyl chlorides—benzoyl chloride and its chloro-, dichloro-, nitro-, and chloronitro- derivatives; salicylsulphonyl chloride; 2-hydroxy-3-naphthoyl chloride—a series of compounds has been obtained, chiefly from 1-amino-7-naphthol, for use in the production of azo- dyes—



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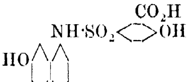

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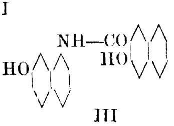


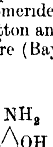
III

The substituted benzoyl derivatives of 1-amino-7-naphthol (I) are crystalline, have definite m.ps. and couple in alkaline solution (Badische, D. R.-P. 283742, 296991, 297414; Eng. P. 13455 of 1914; 8058 of 1915). On reduction with sodium bisulphite, the nitrobenzoyl derivatives furnish *sulphamino-* compounds which not only couple but, by elimination of the SO_3H radicle on treatment with nitrous acid in the cold, can be diazotised (Bayer, D. R.-P. 233117).

The salicylsulphamino- derivatives of 1-amino-7-naphthol, m.p. 257°–258° (II), and 2-amino-7-naphthol, m.p. 217°–218°, couple easily with diazotised bases (Bayer, D. R.-P. 274081, 276331; Eng. P. 3796 of 1914).

Substituted amides of 2-hydroxy-3-naphthoic acid (III) have been obtained from all the aminonaphthols except the 1 : 2-, 2 : 3- and 1 : 8-isomerides; they are taken up by unmordanted cotton and can be coupled with para- red on the fibre (Bayer, D. R.-P. 284997).

AMINONAPHTHOLS.[2]



(i.) 1-**Amino-2-naphthol** (1-*amino-β-naphthol*) is formed when 1-nitroso-β-naphthol is reduced by ammonium sulphide (Stenhouse and Groves,

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[1] β-Naphthol-7-sulphonic acid yields both 7-amino- and 5-amino-β-naphthol (Sachs, *l.c.*).

[2] In this section, which includes the aminonaphthols, aminonaphtholsulphonic acids, and diaminonaphthols, a departure is made from the rule that the numbering indicates the position occupied by the substituted group (NH_2) relatively to the characteristic radicle (OH) of the substance (naphthol) in which substitution is supposed by the name (aminonaphthol) to have occurred. This departure has been made to avoid confusion when German Patents, in which the numbering is given with reference to the amino-group, are consulted. The alternative numbering, based on the rule, is given in brackets.

Chem. Soc. Trans. 1877, 32, 52), or by stannous chloride (Groves, *ibid.* 1884, 45, 296; Paul, Z. angew. Chem. 1897, 10, 48); *or* when 1-nitro-β-naphthol is reduced by tin and hydrochloric acid (Jacobson, Ber. 1881, 14, 806; Zincke, Annalen, 1892, 268, 273).

Preferably, it is obtained when benzeneazo-β-naphthol (Liebermann, Ber. 1883, 16, 286; Groves, *l.c.*), orange II (Liebermann, Ber. 1881, 14, 1311; Witt, Ber. 1888, 21, 3472; Grandmougin and Michel, Ber. 1892, 25, 981; Russig, J. pr. Chem. 1900, [ii.] 62, 55; Paul, *l.c.* 24), or other azo- derivatives of β-naphthol are reduced either by stannous chloride and hydrochloric acid or (Grandmougin, Ber. 1906, 39, 2495) by sodium hypo(hydro)sulphite. Its production electrolytically from Orange II has been described (Boehringer, D. R.-P. 121835; Eng. P. 13542 of 1900), and it can be obtained from its 4-sulphonic acid by means of sodium amalgam (Friedlander and Reinhardt, Ber. 1894, 27, 241).

Properties.—It forms scales, sparingly soluble in boiling water, and in alkaline or ammoniacal solution rapidly becomes brown on exposure to air. The *hydrochloride* B·HCl forms needles (Jacobson, *l.c.*); N-*acetyl* derivative scales, m.p. 235° (Michel and Grandmougin, Ber. 1892, 25, 3433); *diacetyl* derivative, m.p. 116° (Grandmougin, *l.c.*); *dibenzoyl* derivative, silky needles, m.p. 235·5 (Sachs, Ber. 1906, 39, 3024); and *ethyl ether*, prisms, m.p. 51°, b.p. 300°–302° (Cassella, D. P. Anm. C. 2883; Gaess, J. pr. Chem. 1891, [ii.] 43, 27; Paul, Z. angew. Chem. 1896, 9, 620).

Reactions.—It couples in acetic acid solution with diazotised bases forming *azo-* dyes (Aktienges., D. R.-P. 77256; Eng. P. 13833 of 1893). With nitrous acid in the presence of mineral acids diazotisation does not occur, although in neutral solution with copper salts present, *naphthalene*-1-*diazo*-2-*oxide* is obtained (*v.* p. 418). By ferric chloride and other acid oxidising agents, it is converted into [β-] *naphthaquinone* (*cf.* Grandmougin and Michel, *l.c.*, 982).

(ii.) 1-**Amino**-3-**naphthol** [1] (4-*amino-β-naphthol*) is formed when α-naphthylamine-3-sulphonic acid is fused with caustic potash at 250°–260° (Friedlander, Ber. 1895, 28, 1952) or 4-nitro-β-naphthol is reduced by tin and hydrochloric acid (Morgan and Evens, Chem. Soc. Trans. 1919, 115, 1133).

Properties.—It crystallises in needles, decomp. at 185°, is sparingly soluble in water, gives a violet-brown colouration with ferric chloride, and yields easily soluble salts. The N-*acetyl* derivative forms needles, m.p. 179° (Friedländer, *l.c.*); the *dibenzoyl* derivative scales, m.p. 309°–310° (Sachs, Ber. 1906, 39, 3024).

Reactions.—It couples readily with diazotised bases and with nitrous acid gives an unstable *diazo-* compound. By prolonged boiling with acidified water, 1 : 3-*dihydroxynaphthalene* is formed. When heated with aqueous ammonia, it is converted into 1 : 3-*diaminonaphthalene*. On sulphonation with monohydrate at the ordinary temperature, it yields 1-*amino*-3-*naphthol*-4-*sulphonic acid*.

(iii.) 1-**Amino**-4-**naphthol** (4-*amino-α-naphthol*) can be prepared from 4-nitroso-α-naphthol (Grandmougin and Michel, Ber 1892, 25, 976); *or* from 4-nitro-α-naphthol (Liebermann and Dittler, Annalen, 1876, 183, 247); *or* from α-naphthol-orange (Liebermann and Jacobson, Annalen, 1882, 211, 61; Seidel, Ber. 1892, 25, 423; Russig, J. pr. Chem. 1900, [ii.] 62, 30) or other *para*-azo- derivatives of α-naphthol, by reduction with stannous chloride and hydrochloric acid. It is also formed when 4-amino-α-naphthol-2-carboxylic acid is heated at 230°, carbon dioxide being eliminated (Nietzki and Guitermann, Ber. 1887, 20, 1276).

Properties.—It crystallises in very soluble needles, which, when moist, rapidly become blue on exposure to the air; its salts are easily soluble. The N-*formyl* derivative forms rosettes, m.p. 168° (Gaess, D. R.-P. 149022); the N-*acetyl* derivative, crystals, m.p. 178° (Kehrmann and Kissine, Ber. 1914, 47, 3098); the *diacetyl* derivative, prisms, m.p. 158° (Grandmougin and Michel, *l.c.*); the *dibenzoyl* derivative, rhombic crystals, m.p. 215° (Sachs, Ber. 1906, 39, 3026); the N-*dimethyl* derivative, prisms, m.p. 113° (Friedlander and Lagodzinski, *cf.* J. Soc. Chem. Ind. 1897, 16, 793); and the *ethyl ether*, needles, m.p. 96° (Heermann, J. pr. Chem. 1892, [ii.] 45, 545; *cf.* Cassella, D. P. Anm C. 2883).

Reactions. — Oxidising agents, including nitrous acid (*cf.* Badische, D. R.-P. 55404) convert it into [α-]*naphthaquinone*. It does not couple with diazotised bases. Its hydrochloride when heated with methyl or ethyl alcohol under pressure at 170°–180° forms the *monoalkyl ether* of 1 : 4-*dihydroxynaphthalene*. On sulphonation with 10 p.c. anhydro- acid at 30°–40°, it gives 1-*amino*-4-*naphthol*-3-*sulphonic acid*.

1-Acetylamino-4-naphthol (*naphthacetol*), obtained by acetylating the hydrochloride in presence of sodium acetate (Witt, D. R.-P. 90596; Eng. P. 20676 of 1896; Witt and Dedichen, Ber. 1896, 29, 2948) or by shaking diacetyl-1-amino-4-naphthol with caustic soda solution (Kehrmann and Kissine, Ber. 1914, 47, 3097) forms needles, m.p. 187° (W. and D.), 178° (K. and K.), moderately soluble in warm water, and couples in alkaline solution with diazotised bases, giving ortho-*azo-* dyes. The *ethyl ether* (naphthacetin) forms needles, m.p. 189°, almost insoluble in water but soluble in 7·4 parts of boiling alcohol (Henriques, Ber. 1892, 25, 3060; Heermann, *l.c.*).

(iv.) 1-**Amino**-5-**naphthol** (5-*amino-α-naphthol*) can be obtained from α-naphthylamine-5-sulphonic acid by digestion with 60 p.c. caustic soda solution at 240°–250° (Aktienges., D. R.-P. 49448; *cf.* Friedlander and Lagodzinski, J. Soc. Chem. Ind. 1897, 16, 793); *or* from 1 : 5-diaminonaphthalene either by digestion with dilute mineral acids under pressure (*cf.* Aktienges., D. P. Anm. A. 4029), or, in 80 p.c. yield, by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 69, 84; *v.* p. 416). It is also formed from α-naphthol, *or* from α-naphthol-5-sulphonic acid by fusion with sodamide and naphthalene at 190° or 230° respectively (Sachs, D. R.-P. 173522, 181333; Eng. P. 22412 of 1905; Ber. 1906, 39, 3018).

Properties.—In alkaline solution it undergoes little change on exposure to the air. The *hydrochloride* is crystalline, the *dibenzoyl* derivative forms rhombic scales, m.p. 276° (Sachs, *l.c.*), and the N-*dimethyl* derivative, hexagonal tablets, m.p. 112° (Gesellsch., D. R.-P. 50142; Fussgänger, Ber. 1892, 25, 979).

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[1] The 'αγ-aminonaphthol' obtained from β-naphthylamine by nitration, diazotisation and reduction (Gesellsch., D. R.-P. 55059), was probably a mixture of 1-amino-6- and 1-amino-7-naphthol (*cf.* Friedländer and Szymanski, Ber. 1892, 25, 2076).

Reactions.—It can be diazotised (*cf.* Bayer, D. R.-P. 79166) and it couples in acid or alkaline solution with diazotised bases forming *monoazo*-dyes. The *azo*- dye obtained by coupling it with diazotised α-naphthylamine-4-sulphonic acid is not red, as is the case with its isomerides, but cornflower-blue in colour (Sachs, *l.c.*). By prolonged heating with 4 p.c. hydrochloric acid at 180° or by the bisulphite method 1 : 5-*dihydroxynaphthalene* is obtained; but 1 : 5-*diaminonaphthalene* is the product if in the latter process ammonium bisulphite is used instead of the sodium salt. With sulphuric acid in the cold it gives 1-*amino-5-naphthol-6-sulphonic acid*, but with 23 p.c. anhydro- acid at 100° a *disulphonic acid.*

(v.) 1-**Amino-6-naphthol** (5-*amino-β-naphthol*) is formed when 5-nitro-β-naphthol is reduced by stannous chloride and hydrochloric acid (Friedländer and Szymanski, Ber. 1892, 25, 2079); *or* when α-naphthylamine-6-sulphonic acid is fused with caustic alkali (Bayer, D. R.-P. 74060; Eng. P. 11533 of 1892); *or* when 1-amino-6-naphthol-4-sulphonic acid interacts with sodium amalgam (Friedlander and Kielbasinski, Ber. 1896, 29, 1979). It is also formed when β-naphthol, or β-naphthol-6- or 8-sulphonic acid is heated with sodamide and naphthalene at 230° (Sachs, D. R.-P. 173522, 181333; Eng. P. 22412 of 1905; Ber. 1906, 39, 3016).

Properties.—It crystallises in scales, m.p. 186°, shows blue fluorescence in ammoniacal solution, rapidly darkens when moist on exposure to the air, and with ferric chloride gives a dark violet colouration. The N-*acetyl* derivative forms needles, m.p. 215°-216° (Kehrmann and Denk, Ber. 1900, 33, 3296; Sachs. Ber. 1906, 39, 3025); the *diacetyl* derivative, m.p. 187°; the N-*benzoyl* derivative, needles, m.p. 152°; the *dibenzoyl* derivative, needles, m.p. 223°; the *picrate*, yellow needles, m.p. 183° (Sachs, *l.c.*).

Reactions.—It can be diazotised (Sachs, *l.c.*), and it couples in acetic acid or in alkaline solution with diazotised bases (1 or 2 mols.) forming *azo*- dyes.

(vi.) 1-**Amino-7-naphthol** (8-*amino-β-naphthol*) is obtained from 8-nitro-β-naphthol by reduction with stannous chloride and hydrochloric acid (Friedlander and Szymanski, Ber. 1892, 25, 2082); *or* from α-naphthylamine-7-sulphonic acid by digestion with 60 p.c. caustic soda solution at 250° (Cassella, D. R.-P. 69458; Friedlander and Zinberg, Ber. 1896, 29, 41).

Properties.—It crystallises from water in needles, m.p. 206° (Kehrmann and Engelke, Ber. 1909, 42, 351; Cassella, *l.c.*), gives with ferric chloride a greenish-blue colouration, and in acid or alkaline solution shows blue fluorescence. The N-*acetyl* derivative forms tablets, m.p. 165° (Friedländer and Zinberg, *l.c.*); the N-*benzoyl* derivative, crystals, m.p. 208°–209° (Badische, D. R.-P. 296991); the *dibenzoyl* derivative, needles, m.p. 208° (Sachs, Ber. 1906, 39, 3026); and the *ethyl ether*, prisms, m.p. 67°, b.p. 315° (Gaess, J. pr. Chem. 1891, [ii.] 43, 28). For substituted N-*acyl* derivatives used in the production of azo- dyes, *v.* p. 484.

Reactions.—It can be diazotised, and it couples in acetic acid or in alkaline solution with diazotised bases (1 or 2 mols.) forming *azo*-dyes. With sulphuric acid at 20°–30°, it yields 1-*amino-7-naphthol-*(4)-*sulphonic acid*, and at 100°, or with anhydro- acid, a *disulphonic acid.*

(vii.) 1-**Amino-8-naphthol** (8-*amino-α-naphthol*) can be prepared by fusing α-naphthylamine-8-sulphonic acid with caustic alkali at 230°–240° (Badische, D. R.-P. 55404, 62289; Eng. P. 9676 of 1890; Fichter and Gageur, Ber. 1906, 39, 3331); *or* from 1 : 8-diaminonaphthalene either by heating it with dilute mineral acids under pressure (*cf.* Aktienges., D. P. Anm. A. 4029), or by the bisulphite method (Bucherer, J. pr. Chem. 1904, [ii.] 69, 58; *v.* p. 416); *or* by digesting 1 : 8-diaminonaphthalene-4-sulphonic acid with 25 p.c. sulphuric acid, or 1-amino-8-naphthol-5-sulphonic acid with 20 p.c. sulphuric acid under pressure at 135°-140° (Cassella, D. R.-P. 73381). It is also formed when α-naphthol-8-sulphonic acid is heated with sodamide and naphthalene at 230° (Sachs, D. R.-P. 173522; Eng. P. 22412 of 1905; Ber. 1906, 39, 3018).

Properties.—It crystallises in needles, m.p. 95°–97°, is only sparingly soluble in cold, and its *sulphate* in hot water (Badische, *l.c.*; *cf.* Friedlander and Silberstern, Monatsh. 1902, 23, 516). The N-*acetyl* derivative forms needles, m.p. 168°–169°, and couples with diazotised bases; the *diacetyl* derivative, needles, m.p. 118.5°; the N-*benzoyl* derivative, needles, m.p. 193°-194° (Fichter and Gageur, *l.c.*); the N-*dimethyl* derivative, hexagonal tablets, m.p. 112° (Gesellsch., D. R.-P. 50142).

Reactions.—It can be diazotised in dilute solution, but in concentrated solution with excess of nitrite yields also an 8-*amino-*[β-]*naphthaquinoneoxime* in green needles (Fichter and Gageur, *l.c.*; *cf.* Badische, D. R.-P. 62289). In alkaline solution it couples with diazotised bases forming *azo*- dyes. Its sulphite, 1-*amino*-8-*naphthyl sulphite*, formed by boiling it with sodium bisulphite solution (Bucherer, J. pr. Chem. 1904, [ii.] 69, 61), can also be diazotised, and has been used for the production of *azo*-dyes (Badische, D. R.-P. 120690; Eng. P. 13664 of 1900; Bayer, D. R.-P. 211381). With 75 p.c. sulphuric acid at 130°–160°, it gives 1-*amino-8-naphthol-7-sulphonic acid*, but with sulphuric acid at 15°–20° a mixture of this acid with the 5-*sulphonic acid* as chief product and at 100° the 5 : 7-*disulphonic acid.*

(viii.) 2-**Amino-1-naphthol** (2-*amino-α-naphthol*) is obtained by reducing 2-nitroso-α-naphthol with stannous chloride (Liebermann and Jacobson, Annalen, 1882, 211, 55; Grandmougin and Michel, Ber. 1892, 25, 974); *or* 2-nitro-α-naphthol with tin and hydrochloric acid (Liebermann and Dittler, Annalen, 1876, 183, 248); *or* [β-]naphthaquinonephenylhydrazone with sodium hypo(hydro)sulphite (Grandmougin, Ber. 1906, 39, 2496; *cf.* Zincke and Rathgen, Ber. 1886, 19, 2483). It is also formed from 2-amino-1-naphthol-3- or 5-sulphonic acid by interaction with sodium amalgam (Gattermann and Schulze, Ber. 1897, 30, 51).

Properties.—It crystallises in needles, and is only sparingly soluble in cold water. When dissolved in ammonia and shaken with air it gives a green solution, on the surface of which a characteristic violet skin forms (Liebermann and

Jacobson, *l.c.*). The N-*acetyl* derivative forms needles, m.p. 128°–129°, and couples with diazotised bases; the *diacetyl* derivative, needles, m.p. 116° (Grandmougin, *l.c.*); the *ethers* can be diazotised (Grandmougin and Michel, *l.c.*).

Reactions.—Nitrous acid oxidises it to [β-]*naphthaquinone* (Michel and Grandmougin, *ibid.* 3430), but in presence of copper salts converts it in neutral solution into *naphthalene-2-diazo-1-oxide* (*v.* p. 418). On sulphonation with 10 p.c. anhydro-acid at 40°–50° it furnishes a *monosulphonic acid*, which is either the 4- or the 5-derivative (Sandoz, D. R.-P. 69228; Reverdin and de la Harpe, Ber. 1893, 26, 1281).

(ix.) **2-Amino-3-naphthol** (*3-amino-β-naphthol*) is formed from 2 : 3-dihydroxynaphthalene either by heating it with 30 p.c. ammonia solution under pressure at 140°–150° (Hochst, D. R.-P. 73076; Friedlander and Zakrzewski, Ber. 1894, 27, 763), or by the bisulphite reaction (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900; *v.* p. 416). It crystallises in needles, m.p. 234°, sparingly soluble in cold water, and its N-*benzoyl* derivative in hexagonal scales, m.p. 233·5° (Sachs, Ber. 1906, 39, 3024). By coupling it in alkaline solution with diazotised bases, *disazo*- dyes have been obtained (*cf.* Bayer, D. R.-P. 99468; Eng. P. 28090 of 1897).

(x.) **2-Amino-4-naphthol** (*3-amino-α-naphthol*) has been prepared by heating 1 : 3-dihydroxynaphthalene with ammonia under pressure at 130°–140°. Its *hydrochloride* is sparingly soluble; its N-*phenyl* derivative forms needles, and is rapidly oxidised in alkaline solution to [α-]*naphthaquinoneanil*. The *azo*- dyes derived from it resemble closely those from 1 amino-3-naphthol (Friedlander and Rudt, Ber. 1896, 29, 1612).

(xi.) **2-Amino-5-naphthol** (*6-amino-α-naphthol*) can be obtained from β-naphthylamine-5-sulphonic acid by fusion with caustic potash at 260°–270°, but no description of it has been published. On sulphonation it yields a mixture of two *monosulphonic acids*, of which the less soluble constitutes 30 p.c. of the product (Bayer, D. P. Anm. F 7372; Eng. P. 5267 of 1894).

(xii.) **2-Amino-6-naphthol** (*6-amino-β-naphthol*), obtained from 2-amino-6-naphthol-4-sulphonic acid by means of sodium amalgam, crystallises in scales, m.p. 190°–195° (Jacchia, Annalen, 1902, 323, 127), its *dibenzoyl* derivative, in needles, m.p. 233·5° (Sachs, Ber. 1906, 39, 3025); and its *ethyl ether* in pyramids, m.p. 90°–91°, b.p. 330° (Gaess, J. pr. Chem. 1891, [ii.] 43, 48). It gives colour reactions with ferric chloride and many oxidising agents (Sachs, *l.c.* 3028) and couples in alkaline solution with diazotised *o*-aminophenolsulphonic acids forming *monoazo*- dyes (Bayer, D. R.-P. 164516; Eng. P. 18569 of 1902).

(xiii.) **2-Amino-7-naphthol** (*7-amino-β-naphthol*) is formed from β-naphthylamine-7-sulphonic acid by digestion with 50 p.c. caustic soda solution at 260°–300° (Gesellsch., D. R.-P. 47816); *or* from 2 : 7-diaminonaphthalene by the bisulphite reaction (Badische, D. R.-P. 134401; *v.* p. 416); *or* from 2 : 7-dihydroxynaphthalene either by heating it with ammonia under pressure (*cf.* Gesellsch., D. R.-P. 55059), or by the bisulphite method (Franzen and Deibel, J. pr. Chem. 1908, [ii.] 78, 155). It is also obtained, mixed with 1-amino-6-naphthol (Sachs, Ber. 1906, 39, 3017), when β-naphthol-7-sulphonic acid is heated with sodamide and naphthalene at 230° (Sachs, D. R.-P. 173522; Eng. P. 22412 of 1905).

Properties.—It crystallises in needles, m.p. 201° (Franzen and Deibel, *l.c.*, *cf.* Gesellsch., *l.c.*), and is sparingly soluble in water. The N-*acetyl* derivative forms scales, m.p. 220° (Kehrmann and Wolff, Ber. 1900, 33, 1538); the *dibenzoyl* derivative, needles, m.p. 187·5° (Sachs, *l.c.*); the N-*phenyl* derivative, needles, m.p. 160° (Kalle, D. R.-P. 60103; Fischer and Schutte, Ber. 1893, 26, 3087); the N-*salicylsulphamino*-derivative, needles, m.p. 217°–218° (Bayer, D. R.-P. 276331).

Reactions.—It can be diazotised (*cf.* Bayer, D. R.-P. 76166), and it couples in acid or in alkaline solution with diazotised bases forming *azo*- dyes (*cf.* Cassella, D. R.-P. 71329). By the bisulphite method it yields 2 : 7-*diaminonaphthalene*. With sulphuric acid at 30°, it gives *2-amino-7-naphthol-3 : 6-disulphonic acid*.

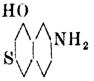
The trimethylammonium chloride, obtained by heating the aminonaphthol in alkaline alcoholic solution with methyl chloride under pressure at 110°, couples with diazotised bases forming *azo*- dyes (Geigy, D. R.-P. 90310).

(xiv.) **2-Amino-8-naphthol** (*7-amino-α-naphthol*), obtained either by fusing β-naphthylamine-8-sulphonic acid with caustic alkali at 260°–270° (Bayer, D. P. Anm. F. 7335; Eng. P. 5148 of 1894), *or* by heating 1 : 7-dihydroxy-β-naphthoic acid with ammonia at 170°–180° (Friedländer and Zinberg, Ber. 1896, 29, 40), crystallises in scales, m.p. 158° (Bayer, *l.c.*), and its N-*acetyl* derivative in needles, m.p. 210°–211° (Friedlander and Zinberg, *l.c.*).

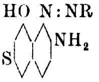
Reactions.—It couples in acetic acid or in alkaline solution with diazotised bases forming *azo*- dyes (Bayer, D. R.-P. 220532; Friedländer and Zinberg, *l.c.*). With sulphuric acid at 20°–30°, it yields a mixture of the 'V' and 'Sch.' *2-amino-8-naphtholmonosulphonic acids*, in about equal amount.

AMINONAPHTHOLSULPHONIC ACIDS.

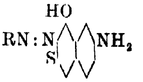
Introductory.—Aminonaphtholsulphonic acids came into use as components of azo- dyes about the year 1889 (*cf.* Cassella, D. R.-P. 55024, 55648; Eng. P. 16699 of 1889), when the discovery was made that certain of them have the property of forming two series of these dyes, tinctorially as well as chemically different in character. Provided the NH_2 and OH radicles be contained in different nuclei, and the position of the sulphonic group or groups be such[1] as to determine the entry of the diazo- complex only into *ortho*- positions relatively to these radicles, coupling in weak acid solution will lead to the production of an azo- dye of type I, and in alkaline solution to one of type II:—



G-acid



I



II

The compounds of type I do not couple further in *acid* solution and cannot be diazotised; those of type II, on the other hand, are diazotisable.

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[1] Compare p. 417.

In many cases monoazo- dyes of either type will couple in *alkaline* solution, to form disazo- dyes, containing the aminonaphtholsulphonic acid as the middle component, but there are exceptions. For example, of the two monoazo- dyes obtained from G-acid (I and II *supra*), only that numbered I can be coupled further under any conditions. This capacity for further coupling cannot be foreseen, and the reasons which promote or inhibit it are unknown.

The chief methods employed for the preparation of these acids are—

(1) Reduction of nitroso- or azo- derivatives, of naphtholsulphonic acids with tin or stannous chloride and hydrochloric acid, or with sodium hypo(hydro)sulphite. By these methods the 1 : 2-, 1 : 4- and 2 : 1-aminonaphtholsulphonic acids are produced.

(2) Digestion of naphthylamine-di- or trisulphonic acids with concentrated caustic alkali solution at 180°–200°. With sulphonic acids from *α-naphthylamine*, the SO_3H group in position 8 is the most easily displaced, then that in 5, the group in 2 or 4 resisting displacement; with acids from *β-naphthylamine*, the SO_3H group in position 4, 5, or 8 is easily displaced, but that in 1 or 6 resists displacement. If the temperature be too high, the amino- group also may be eliminated, and a dihydroxynaphthalenesulphonic acid result from the fusion.

(3) From diaminonaphthalenesulphonic acids either by heating with dilute mineral acids or water under pressure, or by the bisulphite method (*v.* p. 416).

(4) Heating dihydroxynaphthalenesulphonic acids with aqueous ammonia under pressure. With *αβ-dihydroxynaphthalenesulphonic acids*, the OH radicle in the *β*- position is the more easily exchanged for the NH_2 group.

(5) Sulphonation of certain aminonaphthols with sulphuric acid or anhydro acid

Reference to the tables will show that the constitution of most of the acids is known. This has been determined chiefly by a knowledge of the structure of the naphthylaminesulphonic acid employed in the second method, or of the naphtholsulphonic acid the nitroso- or azo-derivative of which is reduced when the first method is used. Confirmatory evidence can be obtained in many cases by a study of the interaction of the acid with sodium amalgam, as SO_3H groups in *α*- positions are more readily eliminated than those in *β*- positions (Friedländer and Lucht, Ber. 1893, 26, 3028); or of the hydrolytic action of 20 p c. hydrochloric acid at the boiling-point, which occurs only when the OH and SO_3H radicles occupy relatively the 1 : 4- position (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 204).

Only scanty information is given in the Patent literature about the properties of the aminonaphtholsulphonic acids and their salts. Apart from their behaviour towards nitrous acid, and towards diazotised bases (*cf.* Cassella, D. R.-P. 82676), these compounds are usually distinguished by the fluorescence or non-fluorescence of solutions of their alkali salts and by the colourations given with ferric chloride or bleaching powder solutions (*cf.* Aktienges., D. R.-P. 68564; Bayer, D. R.-P. 75317). They reduce ammoniacal silver nitrate solution in the cold, and in some cases separate silver from an acid solution of the salt (*cf.* Bayer, D. R.-P. 81621). In the tables which follow, references to fluorescence and to the colourations with bleaching powder solution are usually omitted for want of room.

Allusion has been made to the fact that many of the aminonaphtholsulphonic acids furnish two series of monoazo- dyes, according as coupling takes place in an acid or in an alkaline bath. Among acids of this type are included all that are most valuable for the production of disazo- dyes, as, for example, the G-, J-, and S-monosulphonic, and the B-, H-, and K-disulphonic acids.

The acids derived from 1-amino-8-naphthol, of which all the possible monosulphonic and many disulphonic acids have been prepared, divide themselves into two groups:

(*a*) those which furnish *ortho*-azo- dyes by coupling with diazotised bases, *viz.* the 4- and 5-(or S-)monosulphonic, and the 3 : 5-(or B-), 3 : 6-(or H-) and 4 : 6-(or K-)disulphonic acids, and are of much importance;

(*b*) those, comprising the remainder, which form *para*-azo- dyes and have no industrial value.

Of the other aminonaphtholmonosulphonic acids, mention may be made of those derived from 1 : 2- and 2 : 1-aminonaphthols, which are oxidised in acid solution by nitrous acid, but when diazotised in the absence of free acid furnish *ortho*-hydroxyazo- dyes which are remarkable for their fastness (*v.* p. 418).

By the substitution of alkyl, acyl, or aryl radicles in the NH_2 group, derivatives have been obtained which, by coupling with diazotised bases, furnish valuable monoazo- dyes differing in shade and in degree of fastness from those obtained with the respective aminonaphtholsulphonic acids. These monoazo- dyes belong exclusively to the type numbered II. For an account of some of these derivatives, reference may be made to the following Patents:—

Alkyl (Cassella, D. R.-P. 73128; Eng. P. 5407 of 1893; Geigy, D. R.-P. 91506; Eng. P. 2771 of 1896);

Acetyl (Höchst, D. R.-P. 129000; Eng. P. 17366 of 1898);

Aryl monosulphonic acids (Cassella, D. R.-P. 79084; Eng. P. 11157 of 1894; D. R.-P. 80417; Leonhardt, D. R.-P. 114248; Badische, D. R.-P. 122570; Eng. P. 18726 of 1900); disulphonic acids (Bayer, D. R.-P. 179829; 181929; Eng. P. 5749 of 1906);

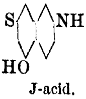
Nitroaryl (Gesellsch., D. R.-P. 101286); *aminoarylacyl* (Gesellsch., D. R.-P. 170045; Bayer, D. R.-P. 233117; 245608; Levinstein, Baddiley and Levinstein, Ltd., Eng. P. 12281 of 1911); *salicylsulphonyl* (Bayer, D. R.-P. 276331); 2 : 3-*hydroxynaphthoyl* (Griesheim, D. R.-P. 296446; Bayer, D. R.-P. 296559).

A series of *ureas* has also been produced by the interaction of phosgene with aminoarylacyl derivatives chiefly of 1-amino-8-naphtholsulphonic acids (Bayer, D. R.-P. 278122; 284938; Eng. P. 9472 of 1914; D. R.-P. 288272; 289107; 289163; 289270; 289271).

J-acid as a source of direct cotton dyes.

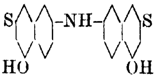
Among the isomeric aminonaphtholsulphonic acids, the chief interest attaches to the 2 : 5 : 7-

or J-acid, which, unlike its isomerides, resembles *para*-diamines (benzidine, &c.) and sulphur bases (dehydrothiotoluidine, primuline, &c.) in endowing most of the azo- dyes of which it is a component with the valuable property of dyeing unmordanted cotton.[1] This fact was recognised first of all[2] in disazo- dyes containing the N-ethyl derivative of J-acid as end component (*cf.* Leonhardt, D. R.-P. 95624; Eng. P. 10699 of 1895; D. R.-P. 98842, 99501), then in those from its N-phenyl derivative, from J-acid itself (Leonhardt, D. R.-P. 114248), and also from 2-amino-5-naphthol-7 : 1-disulphonic acid (Leonhardt, D. R.-P. 117950). Nevertheless, the utilisation of this discovery seems to date from the introduction of direct cotton dyes produced from 5 : 5′-dihydroxy-2 : 2′-dinaphthylamine-7 : 7′-disulphonic acid (I *infra*) by coupling with diazotised aniline, toluidine, &c. (Bayer, D. R.-P. 114841; Eng. P. 24296 of 1899), followed by a series of direct cotton monoazo- dyes (Bayer, D. R.-P. 122905; Eng. P. 2683 of 1900), disazo- dyes (Bayer, D. R.-P. 129494; Gesellsch., D. R.-P. 126802), and trisazo- dyes (Bayer, D. R.-P. 121867; Eng. P. 3673 of 1900) obtained from J-acid itself.



J-acid.

Experience showed that the affinity for unmordanted cotton was increased by the substitution of acyl radicles in the amino- group of J-acid,[3] and, of the many derivatives examined, the azo- dyes from the substituted ureas (II) gave, perhaps, the best results in this respect.



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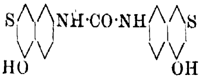
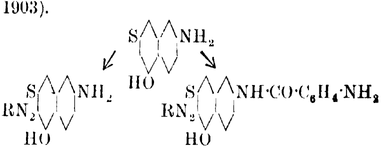


II

But these dyes, although pure in shade and fast to acids, were less fast to alkalis. By the transference of the diazotisable amino- group in the monoazo- dyes of J-acid from the naphthalene nucleus to a benzene ring present in the acyl radicle (III), fastness to alkalis also was secured (*cf.* Gesellsch., D. R.-P. 151017; Eng. P. 13778 of 1902; D. R.-P. 170045; Eng. P. 24936 of 1903).



III

These aminoarylacyl-2-amino-5-naphthol-7-sulphonic acids, when coupled in alkaline solution, give monoazo- dyes which can be diazotised on the fibre, and, without any essential alteration in shade, developed with β-naphthol and thereby rendered fast to washing.[4] By appropriate substitution, therefore, it is possible to obtain from J-acid direct cotton dyes of any desired degree of intensity, purity of shade, or fastness.

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[1] Certain disazo-dyes, with J-acid as middle component and nitro-*o*-diazophenols as end components, are unsuitable for dyeing unmordanted cotton (Oehler, D. R.-P. 151332, Eng. P. 8575 of 1903).

[2] J-acid, obtained from Armstrong and Wynne's β-naphthylamine-5 : 7-disulphonic acid (Badische, D. R.-P. 75469; Eng. P. 2614 of 1893), was employed originally for the production of direct cotton dyes by coupling with diazotised *para*-diamines (*ibid.*) or with dehydrothiotoluidine (*cf.* Bayer, D. R.-P. 88846; 92708; Eng. P. 10629 of 1894), its specific cotton-fixing capacity being thereby obscured.

[3] The following acyl and other derivatives have been studied in this connexion, $R\,NH_2$ being J-acid in the amino- group of which substitution has occurred:

$R\cdot NH\cdot CO\cdot CH_3$ (Bayer, D. R.-P. 119828; Eng. P. 2683 of 1900).

$R\cdot NH\cdot CO\cdot C_6H_5$ (Bayer, D. R.-P. 127141).

$R\cdot NH\cdot C(NH)\cdot NH\,R$ (Bayer, D. R.-P. 129417; 132537, Eng. P. 18939 of 1900).

$R\cdot NH\cdot CO_2\cdot Alk$ (Badische, D. R.-P. 221967).

$R\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot R$ (Bayer, D. R.-P. 1[illegible]6443, 128195; Eng. P. 18939 of 1900).

$R\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot R$ (Bayer, D. R.-P. 129478, 126801; Eng. P. 18939 of 1900).

$R\cdot NH\cdot CS\cdot NH\cdot R$ (Bayer, D. R.-P. 116201, 122286, 126133, 123886; Eng. P. 3615, 12899 of 1900).

$R\cdot NH\cdot CO\cdot NH\,R$ (Bayer, D. R.-P. 116200, 122904, 123693; Eng. P. 3615, 12899 of 1900).

$R\cdot NH\cdot CO\cdot C_6H_4\cdot CO\cdot NH\,R$ (Hochst, D. R.-P. 268068).

$R\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2$ (Gesellsch., D. R.-P. 151017; Eng. P. 13778 of 1902).

$R\cdot NH\cdot CO\cdot C_6H_4\,NH\cdot CO\cdot C_6H_4\cdot NH_2$ (Bayer, D. R.-P. 230595, 240827; Eng. P. 14735 of 1910).

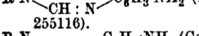
$R\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot NH\,CO\cdot CH_3$ (Gesellsch., D. R.-P. 148505).

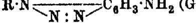
$R\cdot NH\cdot SO_2\cdot C_6H_3(OH)\cdot CO_2H$ (Bayer, D. R.-P. 276331).

$R\cdot NH\cdot CO\cdot C_{10}H_6\cdot OH$ [2 : 3] (Griesheim, D. R.-P. 295767).

$R\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH_2$ (Bayer, D. R.-P. 254510).

$R\cdot N(C_6H_5)\cdot CO\cdot H$ (Bayer, D. R.-P. 245608).

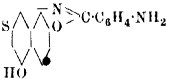

$R\cdot N\overset{\rule{4em}{0.4pt}}{\underset{CH\,:\,N}{\diagdown\qquad\diagup}}C_6H_3\cdot NH_2$ (Höchst, D. R.-P. 252575; 255116).


$R\cdot N\overset{\rule{4em}{0.4pt}}{\underset{N\,:\,N}{\diagdown\qquad\diagup}}C_6H_3\cdot NH_2$ (Gesellsch., D. R.-P. 214658).

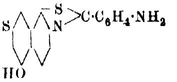
Acridine derivative (Höchst, D. R.-P. 272612).

Carbazole derivative (Kalle, D. R.-P. 228959; Eng. P. 8127 of 1910).

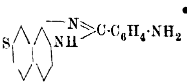
[4] In addition to J-acid and its N-derivatives, the following azoles, which do not fall within the scope of this article, also furnish substantive dyes for cotton under similar conditions, and with them the same method for securing fastness of the dyestuff to alkalis is used.



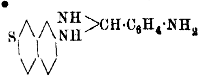
(Bayer, D. R.-P. 165102; Eng. P. 1675 of 1905),



(Bayer, D. R.-P. 166903; Eng. P. 27843 of 1904; D. R.-P. 235051);



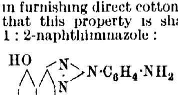
(Aktienges., D. R.-P. 167139; Eng. P. 11759 of 1905; Bayer, D. R.-P. 172319; Eng. P. 1675 of 1905);



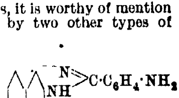
(Cassella, D. R.-P. 209110);

and a corresponding aminophenyl derivative of 1 : 2-naphthatriazine-5-hydroxy-7-sulphonic acid (Cassella, D. R.-P. 191024; Eng. P. 14787 of 1905).

While it may not be a matter for surprise that these five types of compound should resemble J-acid in furnishing direct cotton dyes, it is worthy of mention that this property is shared by two other types of 1 : 2-naphthiminazole:



(Gesellsch., D. R.-P. 146375);



(Cassella, D. R.-P. 233939; Eng. P. 15646 of 1910);

although the aminonaphtholsulphonic acids—2 : 8 : 6 (G-acid) or 2 : 8 : 3 : 6 (2R-acid) and 2 : 3 : 6 (R-acid)—to which respectively they are constitutionally related do not exhibit it.

Aminonaphtholmonosulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S		
1 : 2 : 4	(1) Reduction of nitroso-β-naphthol with sulphurous acid (Boniger, Ber. 1894, 27, 23; *Tomioka, cf J Soc Chem. Ind* 1917, 36, 1043) or with sodium hypo(hydro)-sulphite (Grandmougin, Ber 1906, 39, 2497). (2) Action of sodium bisulphite on [β-]naphthaquinone-α-chlorimide (Friedlander and Reinhardt, Ber. 1894, 27, 241. Tomioka, *l c.*). (3) Fusion of α-naphthylamine-2 : 4-disulphonic acid with caustic alkali (Tomioka, *l c*).	*Acid*, $HA + \frac{1}{2}H_2O$, very sparingly soluble needles; *sodium* salt, NaA, needles. In alkaline solution either alone or condensed with [β-]naphthaquinone yields dyestuffs by oxidation with air (Dahl, D R.-P. 82097; 82740; **Eng. P.** 5153 of 1895). Diazotisable, in absence of mineral acids, giving *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024; **Eng. P.** 10235 of 1904; *v.* p. 418).
1 : 2 : 5	Reduction of azo-derivatives of β-naphthol-5-sulphonic acid (Witt, Ber. 1888, 21, 3478).	*Acid*, very sparingly soluble. Gives brown colouration with ferric chloride.
1 : 2 : 6	(1) Reduction of nitroso-β-naphthol-6-sulphonic acid by tin and hydrochloric acid (Meldola, Chem. Soc. Trans 1881, 39, 47) (2) Reduction of azo-derivatives of β-naphthol-6-sulphonic acid (Witt, Ber. 1888, 21, 3475).	*Acid*, HA, sparingly soluble needles; *sodium* salt (*Eikonogen*), $NaA + 2\frac{1}{2}H_2O$. Solutions, especially if alkaline, are very sensitive to air. Gives brown colouration with ferric chloride. For *diazo-oxide*, *cf* Geigy, *l.c* : *v* p. 418 Couples with diazotised bases (*cf* Aktienges., D. R-P 79103, Eng P. 13833 of 1893).
1 : 2 : 7	Reduction of azo-derivatives of β-naphthol-7-sulphenic acid (Witt, Ber. 1888, 21, 3477).	*Acid*, very sparingly soluble needles. Gives brown colouration with ferric chloride. For *diazo-oxide*, *cf.* Geigy, *l c* ; *v.* p. 418. Couples with diazotised bases (*cf.* Aktienges., *l.c.*).
1 : 2 : 8	Reduction of azo-derivatives of β-naphthol-8-sulphonic acid (Witt, Ber. 1888, 21, 3474).	*Acid*, very sparingly soluble leaflets Gives brown colouration with ferric chloride. For *diazo-oxide* *cf.* Geigy, *l c* ; *v.* p 418.
1 : 3 : 4 [4 : 2 : 1]	1 - Amino - 3 - naphthol sulphonated with monohydrate (Friedlander and Rudt, Ber. 1896, 29, 1609).	*Acid*, very sparingly soluble needles. Converted by water at 120° into 1 . 3-*dihydroxynaphthalene*.
1 : 3 : 6 [4 : 2 : 7]	Mixed with 1 : 6 : 3-acid, by boiling α-naphthylamine-3 . 6-disulphonic acid with 75 p c caustic potash solution (Casella, D. R-P. 82676).	*Acid*, very sparingly soluble; *sodium* salt separated by salting out from the 1 ; 6 : 3-isomeride. Forms a readily soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (Cassella, *l.c.*).
1 : 4 : 2 [4 : 1 : 3]	Reduction of nitroso- or azo- derivatives of α-naphthol-3-sulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1281).	No description published
1 : 4 : 3 [4 : 1 : 2]	(1) 1-Amino-4-naphthol sulphonated with 10 p c anhydro-acid at 30°–40° (Seidel, Ber. 1892, 25, 424; *cf.* Friedländer and Reinhardt, Ber. 1894, 27, 239). (2) Reduction of nitroso- (Conrad and Fischer, Annalen, 1893, 273, 114) or of azo-derivatives (Reverdin and de la Harpe, Ber. 1892, 25, 1403) of α-naphthol-2-sulphonic acid	*Acid*, HA, very sparingly soluble needles, which give a grass-green solution in alkalis or alkali carbonates, rapidly becoming brown. Oxidised by dilute nitric acid to [α-]*naphthaquinone-3-sulphonic acid* and *phthalic acid*; by permanganate in alkaline solution to *phthalic acid* (Seidel, *l c.*).
1 : 4 : 5 [4 : 1 : 8]	(1) Reduction of azo-derivatives of α-naphthol-8-sulphonic acid (Reverdin and de la Harpe, Ber 1892, 25, 1404) (2) Electrolytic reduction of α-nitronaphthalene-5-sulphonic acid in sulphuric acid solution (Gattermann. Ber. 1893, 26, 1852; Bayer, D. R.-P. 81621).	*Acid*, leaflets soluble in water but insoluble in cold alcohol, solution in ammonia yellow; *lead* and *barium* salts, sparingly soluble in water (Bayer, *l.c*).
1 : 4 : 6 [4 : 1 : 7]	Electrolytic reduction of α-nitronaphthalene-6-sulphonic acid in sulphuric acid solution (Bayer, D. R.-P. 81621).	*Acid*, needles soluble in water or cold alcohol, solution in ammonia yellow; *lead* and ***barium*** salts soluble in water (Bayer, *l.c.*).
1 : 4 : 7 [4 : 1 : 6]	Electrolytic reduction of α-nitronaphthalene-7-sulphonic acid in sulphuric acid solution (Bayer, D. R.-P. 81621).	*Acid*, needles soluble in water or cold alcohol, solution in ammonia yellow; *lead* and ***barium*** salts soluble in water (Bayer, *l,c.*).
1 : 5 : 2 [5 : 1 : 6]	(1) α-Naphthylamine-2 : 5-disulphonic acid digested with 50 p c. caustic soda solution at 240°–270° (Landshoff, Eng. P. 6195 of 1890; D. P. Anm. C. 4479). (2) From 1 : 5-diaminonaphthalene-2-sulphonic acid by the bisulphite reaction (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 213; *v.* p. 416).	*Acid*, sparingly soluble needles Gives green colouration with ferric chloride (*cf.* Bayer, D. R.-P. 75317). Forms a sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676).

Constitution.	Preparation.	Acids, Salts and Reactions.
N:O:S		
1 : 5 : 4 [5 : 1 : 8]	(1) From 1-acetylamino-5-aminonaphthalene-4-sulphonic acid; or from (2) 1 : 5-dihydroxynaphthalene-4-sulphonic acid by the bisulphite reaction (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 223; *v.* p. 416).	*Acid*, HA, crystallises in needles. Couples with diazotised bases forming *azo*-dyes.
1 : 5 : 6 [5 : 1 : 2]	1-Amino-5-naphthol sulphonated with sulphuric acid below 100° (Aktienges., D. R.-P. 68564).	*Acid*, very sparingly soluble needles. Gives blue colouration with ferric chloride. Forms greenish-yellow solution with nitrous acid. Couples with diazotised bases.
1 : 5 : 7 [5 : 1 : 3] **M-acid.**	(1) *a*-Naphthylamine-5 : 7-disulphonic acid heated with 75 p.c. caustic soda solution at 170° (Badische, D. R.-P. 73276; Eng. P. 2370 of 1893). (2) 1 : 5-Diaminonaphthalene-3-sulphonic acid heated with water under pressure at 160° (Cassella, D. R.-P. 85058). (3) From 1 : 5-dihydroxynaphthalene-7-sulphonic acid by the bisulphite reaction (Badische, D. R.-P. 117471; Eng. P. 1387 of 1900, *v.* p. 416). (4) 1-Amino-5-naphthol-2 : 7-disulphonic acid heated with 10 p.c. sulphuric acid under pressure at 135° (Cassella, D. R.-P. 188505).	*Acid* and *sodium* salt, sparingly soluble leaflets. Gives black colouration with ferric chloride. Forms a deep orange-yellow sparingly soluble *diazo*-compound (*cf.* Cassella, D. R.-P. 82676). Couples in alkaline solution with diazotised bases (*cf.* Badische, D. R.-P. 75327, 82572; Eng. P. 2370 of 1893).
1 : 5 : 8 [5 : 1 : 4]	From 1 : 5-diaminonaphthalene-4-sulphonic acid by the bisulphite reaction (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 226; *v.* p. 416).	*Acid*, $HA+3\frac{1}{2}H_2O$. Couples with diazotised bases forming *azo*-dyes.
1 : 6 : 3 [6 : 2 : 7]	(1) Mixed with 1 : 3 : 6-acid, by boiling *a*-naphthylamine-3 : 6-disulphonic acid with 75 p.c. caustic potash solution (Cassella, D. R.-P. 82676). (2) 1-Amino-6-naphthol-3 : 5-disulphonic acid boiled with dilute acids (Cassella, D. P. Anm. C. 5163).	*Acid*, sparingly soluble; *sodium* salt readily soluble. Forms a yellow sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676).
1 : 6 : 4 [5 : 2 : 8]	*a*-Naphthylamine-4 : 6-disulphonic acid fused with caustic soda at 180°–200° (Dahl, D. R.-P. 68232; Friedländer and Kielbasinski, Ber. 1896, 29, 1979).	*Acid*, sparingly soluble needles; *sodium* salt, NaA, needles; *barium* salt, prisms, readily soluble. Gives brownish colouration with ferric chloride. Forms a sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676).
1 : 7 : 3 [8 : 2 : 6] **B-acid.**	Mixed with a more soluble isomeride, by heating *a*-naphthylamine-3 : 7-disulphonic acid with 10 p.c. caustic soda under pressure at 200° (Cassella, D. R.-P. 57007, 58352).	*Acid*, very sparingly soluble needles; *sodium* salt readily soluble leaflets. Forms a very sparingly soluble *diazo*-compound. Couples with diazotised bases, giving two series of *monoazo*-dyes (Cassella, *l.c.*).
1 : 7 : (4) [8 : 2 : (5)]	1-Amino-7-naphthol sulphonated with sulphuric acid below 30° (Cassella, D. R.-P. 75066).	*Acid*, sparingly soluble; *alkali* salts readily soluble. Forms a sparingly soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Cassella, *l. c.*; Bayer, D. R.-P. 198138).
1 : 8 : 2 [8 : 1 : 7]	(1) *a*-Naphthylamine-2 : 8-disulphonic acid fused with caustic soda at 170°–220° (Cassella, D. R.-P. 75710). (2) 1-Amino-8-naphthol-2 : 4-disulphonic acid boiled with 50 p.c. sulphuric acid (*ibid.*)	*Acid*, sparingly soluble radiate prisms. Forms a dark brown sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676).
1 : 8 : 3 [8 : 1 : 6]	(1) *a*-Naphthylamine-3 : 8-disulphonic acid fused with caustic alkali below 210° (Bayer, D. P. Anm. F. 4723; Eng. P. 13443 of 1890). (2) 1-Amino-8-naphthol-3 : 5-disulphonic acid boiled with dilute sulphuric acid at 140° (Leonhardt, D. P. Anm. F. 8626; Eng. P. 19253 of 1895; Cassella, D. R.-P. 108848).	*Acid*, sparingly soluble prisms or needles; *sodium* salt readily soluble. Forms an orange-yellow sparingly soluble *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 82676).
1 : 8 : 4 [8 : 1 : 5] **S-acid.**	(1) *a*-Naphthylamine-4 : 8-disulphonic acid fused with caustic alkali at 210° (Badische, D. R.-P. 63074; Eng. P. 20275 of 1891; Bayer, D. R.-P. 75317). 2) From 1 : 8-diaminonaphthalene-4-sulphonic acid by the bisulphite method in presence of acetone (Badische, D. R.-P. 120016; Eng. P. 16921 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 70, 349; *v.* p. 416).	*Acid*, sparingly soluble needles; *alkali* salts readily soluble, showing bluish-green fluorescence in solution (Bayer, *l. c.*). Gives emerald-green coln. with ferric chloride (*ibid.*). Forms an orange sparingly soluble *diazo*-compound *cf.* Cassella, D. R.-P. 82676) Couples in acid or in alkaline solution with diazotised bases, being used as middle component for *disazo*-dyes (*cf.* Badische, D. R.-P. 91855; Eng. P. 9894 of 1893). For *acetyl*, *aryl*, and *nitroaryl* derivatives, see p. 488.

Constitution.	Preparation.	Acids, Salts and Reactions
N : O : S **1 : 8 : 5** [8 : 1 : 4]	(1) From 1 : 8-diaminonaphthalene-5-sulphonic acid either by boiling with 20 p.c. sulphuric acid (Cassella, D. R.-P. 73607, Eng. P. 4613 of 1893), or by the bisulphite method (Bayer, D. R.-P. 109102; Eng. P 16807 of 1899; *v.* p. 416) (2) α-Naphthylamine-5 · 8-disulphonic acid heated with 75 p.c. caustic potash solution at 150° (Bayer, D. R.-P. 75055; Eng. P 15269 of 1893). (3) 8-Chloro - α - naphthylamine-5-sulphonic acid heated with 50 p.c. caustic soda solution under pressure at 190° (Badische, D. R.-P. 112778) (4) Mixed with 1 . 8 : 7 acid, when 1-amino-8-naphthol is sulphonated with sulphuric acid at 15°–20° (Badische, D. R.-P. 62289; Eng. P. 9676 of 1890; D. R.-P. 77937; 84951).	*Acid*, very sparingly soluble needles; ***sodium*** and ***potassium*** salts readily soluble, showing violet fluorescence in solution (Cassella, *l.c.*). The *calcium* salt is easily soluble (Badische, D. R.-P. 77937). Gives dirty green colouration with ferric chloride (Bayer, D. R.-P. 75055). Forms a readily soluble yellow *diazo*-compound (Cassella, *l.c.*). Couples in acid or in alkaline solution with diazotised bases, being used as a middle component for *disazo*-dyes (*cf.* Badische, D. R.-P. 81241; 114906) For *benzoyl* derivative and *azo*-dyes therefrom, *cf.* Badische, D. R.-P. 54662; Eng. P. 9676 of 1890.
1 : 8 : 6 [8 : 1 : 3] **H-acid.**	(1) 1 · 8 - Diaminonaphthalene - 3 - sulphonic acid heated with 15 p.c. sulphuric acid at 120° (Cassella, D. R.-P. 70780, Eng. P 6972 of 1891; *cf.* Cassella, D. R.-P. 73607). (2) α-Naphthylamine-6 8-disulphonic acid heated with 50 p.c. caustic potash solution under pressure at 200° (Bayer, D. R.-P. 80853; Eng. P 15269 of 1893). (3) 1-Amino-8-naphthol-4 . 6-disulphonic acid boiled with zinc-dust and dilute caustic soda solution (Kalle, D. R.-P. 233934)	*Acid*, sparingly soluble needles; *sodium* and ***potassium*** salts readily soluble; *barium* salt, needles (Bayer, *l.c.*) Gives green colouration with ferric chloride (Bayer, *l.c.*). Forms a yellow sparingly soluble *diazo*-compound (Bayer, *l.c.*) Couples in alkaline solution with diazotised bases (*cf.* Bayer, D. R.-P. 82074; 85389; Eng. P. 15269 of 1893).
1 : 8 : 7 [8 : 1 : 2]	1-Amino-8-naphthol sulphonated with 75 p.c. sulphuric acid at 130°–160° (Badische, D. R.-P. 82900), *or* (mixed with 1 8 . 5-acid) with sulphuric acid at 15°–20° (Badische, D. R.-P. 84951)	*Acid*, sparingly soluble; *acid calcium* salt almost insoluble Forms a readily soluble *diazo*-compound. Couples with diazotised bases.
2 : 1 : 3	Reduction of azo-derivatives of α-naphthol-3-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 54)	*Acid*, HA, broad needles.
2 : 1 : 4[1]	(1) Reduction of azo- (Konig, Ber. 1890, 23, 808) *or* nitroso- derivatives of α-naphthol-4-sulphonic acid (Witt and Kaufmann, Ber. 1891, 24, 3162). (2) Action of sodium bisulphite on 2-nitroso-α-naphthol (Schmidt, J. pr. Chem. 1891, [ii.] 44, 531; *cf.* Boniger, Ber. 1894, 27, 29) *or* [β-]naphthaquinone-β-chlorimide (Friedlander and Reinhardt, Ber. 1894, 27, 242).	*Acid*, HA, sparingly soluble needles (Friedländer and Reinhardt, *l.c.*). Forms a violet-black dyestuff by oxidation with air (Reverdin and de la Harpe, D. R.-P. 63043; Eng. P. 16377 of 1891). Not diazotisable in acid solution (*cf.* Cassella, D. R.-P. 82676), but in absence of acid, gives *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024; Eng. P. 10235 of 1904; *v.* p. 418).
2 : 1 : 5[1]	Reduction of azo-derivatives of α-naphthol-5-sulphonic acid (Gattermann and Schulze, Ber. 1897, 30, 51; *cf.* Reverdin and de la Harpe, Ber. 1893, 26, 1280)	*Acid*, HA, sparingly soluble scales or needles. Diazotisable in absence of free mineral acid giving *diazo-oxide* (*cf.* Geigy, 171024; Eng. P. 10235 of 1904; *v.* p. 418).
2 : 1 : 7	Reduction of 2-nitro-α-naphthol-7-sulphonic acid (Finger, J. pr. Chem. 1909, [ii.] 79, 444).	*Acid*, HA + $2H_2O$, needles; alkaline solution becomes dark green on exposure to the air.
2 : 3 : 6 [3 : 2 : 7] **R-acid.**	(1) α-Naphthylamine-3 : 6-disulphonic acid heated with 75 p.c. caustic soda at 230°–250° (Hochst, D. R.-P. 53076: Eng. P. 15176 of 1889; Friedlander and Zakrzewski, Ber. 1894, 27, 763). (2) 2 . 3-Dihydroxynaphthalene-6-sulphonic acid heated with ammonia at 150°–160° (Aktienges., D. R.-P. 62964; *cf.* Oesterreich, J. Soc. Chem. Ind. 1898, 17, 836).	*Acid*, very sparingly soluble needles; *sodium* salt leaflets; *barium* salt, BaA_2, sparingly soluble. Gives dark blue colouration with ferric chloride (Hochst, *l.c.*). Forms an orange *diazo*-compound (*cf.* Höchst, *l.c.*; Cassella, D. R.-P. 109932; Eng. P. 28107 of 1897). Couples in alkaline solution with diazotised bases (*cf.* Aktienges., D. R.-P. 84145).
2 : 4 : 6 [3 : 1 : 7]	α-Naphthol-3 . 7-disulphonic acid heated with ammonia under pressure at 180° (Kalle, D. R.-P. 94079).	*Acid*, sp. sol. leaflets; *alkali* salts readily soluble. Forms a yellow *diazo*-compound. Couples with diazotised bases.
2 : 4 : 7 [3 : 1 : 6]	(1) β-Naphthylamine-4 : 7-disulphonic acid heated with 35 p.c. caustic alkali at 200° (Bayer, D. P. Anm. F. 7978; Eng. P. 25214 of 1894). (2) α-Naphthol-3 : 6-disulphonic acid heated with ammonia under pressure at 180° (Kalle, D. R.-P. 94079).	*Acid*, moderately soluble leaflets; *alkali* salts readily soluble. Forms a yellow *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Bayer, *l.c.*).

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[1] An acid containing the sulphonic group in either the 4- or the 5- position is produced when 2-amino-1-naphthol is sulphonated with 10 p.c. anhydro-acid at 40°. It is sparingly soluble and gives a brown colouration with ferric chloride (Reverdin and de la Harpe, Ber. 1893, 26, 1280; Kern and Sandoz, D. R.-P. 69228).

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S **2 : 4 : 8** [3 : 1 : 5]	β-Naphthylamine-4 : 8-disulphonic acid fused with 80 p.c. caustic alkali at 215° (Bayer, D P. Anm. F. 8070; Eng. P. 3580 of 1895).	*Acid*, sp sol. needles ; *alkali* salts easily soluble. Gives no colouration with ferric chloride. Forms a yellow sp. sol. *diazo*-compound. Couples in alkaline solution with diazotised bases.
2 : 5 : (6) [6 : 1 : (2) and **2 : 5 : (8)** [6 : 1 : (4)]	2-Amino-5-naphthol sulphonated with sulphuric acid at 20° 30° (Bayer, D P Anm. F. 7372, Eng. P. 5267 of 1894) forms two acids, about which little is known, the yield of the less soluble being 30 p.c.	One of the acids gives a dirty precipitate, the other, a bluish-grey precipitate with ferric chloride. Each acid forms a yellow *diazo*-compound and couples with diazotised bases.
2 : 5 : 1 [6 : 1 : 5]	β - Naphthylamine - 1 : 5 - disulphonic acid fused with caustic alkali at 210°–230° (Kalle, D. R.-P. 233105 ; 242052 ; Eng P 9743 ; 9744 of 1910).	*Acid*, moderately soluble needles. Gives brownish-red *diazo*-compound. Couples in alkaline solution. In acid solution loses its SO_3H group in coupling.
2 : 5 : 7 [6 : 1 : 3] **J-acid.**	(1) β-Naphthylamine-5 : 7-disulphonic acid fused with caustic alkali at 180°, or digested with 50 p c. caustic soda solution under pressure at 190° (Badische, D. P. Anm B. 14154 ; D. R -P. 75469 ; Eng P. 2614 of 1893) (2) From 1 6-dihydroxynaphthalene-3-sulphonic acid by the bisulphite method (Badische, D. R -P 117471 ; Eng. P. 1387 of 1900 ; *v*. p. 416)	*Acid*, sparingly soluble ; *alkali* salts readily soluble. Gives no colouration with cold, but a brownish-black precipitate with hot ferric chloride (*cf.* Badische, D. R.-P. 73276). Forms a yellow *diazo*-compound Couples in acid or alkaline solution with diazotised bases forming two series of *monoazo*-dyes. 1-*Chloro*- or 1-*bromo*-J-acid (Bayer, D. R.-P. 254715 ; 258299 ; Eng. P. 14152 ; 14153 of 1912). For *alkyl*, *aryl*, and other derivatives, *v*. p. 489.
2 : 5 : 8 [6 : 1 : 4]	1 : 6-Dihydroxynaphthalene-4-sulphonic acid heated with 28 p c ammonia under pressure at 140°–180° (Dahl, D. R.-P. 70285 ; Eng P. 4110 of 1892)	*Acid*, sparingly soluble ; *alkali* salts readily soluble. Gives brown colouration with ferric chloride. Forms a yellow sp. sol. *diazo*-compound. Couples in acid or in alkaline solution with diazotised bases (Dahl, *l c.* ; D. R -P. 67258).
2 : 6 : 4 [6 : 2 : 8]	Reduction of 6-nitro-β-naphthol-8-sulphonic acid (Jacchia, Annalen, 1902, 323, 124).	*Acid*, HA + H_2O, sparingly soluble needles. Forms a yellow sp. sol. *diazo*-compound.
2 : 7 : (3) [7 : 2 : (6)] **F-acid.**	2 : 7-Dihydroxynaphthalenesulphonic acid heated with 30 p c ammonia under pressure at 120°-150° (Aktienges., D. R.-P. 63956).	*Acid*, very sp. sol ; *alkali* salts easily soluble. Gives greenish-black colouration with ferric chloride. Forms a yellow sp sol. *diazo*-compound. Couples in acid or in alkaline solution with diazotised bases.
2 : 7 : ? [7 : 2 : ?]	Partial hydrolysis of the disulphonic acid formed from 2-amino-7-naphthol by sulphonation with sulphuric acid at 30° (Cassella, D. R -P. 131526).	*Acid*, needles ; *sodium* salt, NaA + H_2O, sp. soluble. Gives violet precipitate with ferric chloride. Forms a yellow sp. sol *diazo*-compound. Couples in acid or in alkaline solution with diazotised bases, giving two series of *monoazo*-dyes.
2 . 8 : (5) [7 : 1 : (4)] **2 : 8 . (7)** [7 : 1 : (2)]	2-Amino-8-naphthol sulphonated with sulphuric acid at 30° forms two acids in about equal proportion (Bayer, D. P. Anm. F. 7335 ; Eng. P. 5148 of 1894).	' *Sch* ' *acid*, readily, ' *V* ' *acid*, sp. sol. ; separated by adding acid to soln of mixed calcium salts. Each acid forms a yellow soluble *diazo*-compound and couples with diazotised bases.
2 : 8 : 6 [7 : 1 : 3] **G-acid.**	(1) β-Naphthylamine-6 . 8-disulphonic acid heated with 50 p c caustic soda solution at 190°–195° (Cassella, Eng P. 16699 ; D P. Anm. C 3063 ; *cf* Hoechst, D. R.-P. 53076 ; Eng. P. 15176 of 1889). (2) From 1 : 7-dihydroxynaphthalene-3-sulphonic acid either by heating with 30 p c ammonia under pressure at 120°–150° (Aktienges , D R.-P. 62964), *or* by the bisulphite reaction (Bucherer, J. pr. Chem. 1904, [II.] 69, 89 ; *v*. p. 416).	*Acid*, very sp sol. needles ; *alkali* and *alkaline earth* salts, readily sol , *lead* salt, sp. sol. needles (Tauber and Walder, Ber. 1896, 29, 2268). Gives dirty claret colouration with ferric chloride. Forms a yellow sp. soluble *diazo*-compound. Couples in acid or in alkaline solution, forming two series of *monoazo*-dyes, *v*. p. 487). 1 - *Chloro*- or 1 - *bromo* - G - acid (Bayer, D. R. - P. 254715 , Eng. P. 14152 of 1912). For *alkyl*, *acetyl*, *aryl*, &c., derivatives. *v*. p. 488.

Aminonaphtholdisulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S : S **1 : 2 : 3 : 6**	Reduction of azo-derivatives of β-naphthol-3 : 6-disulphonic acid (Witt, D. R.-P. 49857 ; Ber. 1888, 21, 3479).	*Acid sodium* salt, NaHA, readily soluble needles. Gives dark brown colouration with ferric chloride. Diazotisable in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy, D. R.-P. 171024 ; *v.* p. 418). Does not couple with diazotised bases.
1 : 2 : 3 : 7	Reduction of 1-nitroso-β-naphthol-3 : 7-disulphonic acid (Geigy, D. R.-P. 171024 ; Eng. P. 10235 of 1904).	*Acid*, sp. sol. ; alkaline solutions greenish-yellow. Diazotisable in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy, *l.c.* ; *v.* p. 418).
1 : 2 : 4 : 6	Interaction of 1-nitroso-β-naphthol-6-sulphonic acid and sulphurous acid (Boniger, Ber. 1894, 27, 3052).	*Acid sodium* salt, NaHA, readily soluble needles. Diazotisable in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy, *l.c.* ; *v.* p. 418).

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S : S		
1 : 2 : 4 : ?	Sulphonation of 1-amino-2-naphthol-4-sulphonic acid with monohydrate below 100° (Griesheim, D. P. Anm. C. 15414 ; 15820 ; Eng. P. 3655 of 1908).	*Acid sodium* salt, NaHA, very soluble, shows in solution bluish-green fluorescence like the acid sodium salt of the 4 : 6-disulphonic acid, with which it may be identical.
1 : 2 : 4 : 7	Interaction of 1-nitroso-β-naphthol-7-sulphonic acid and sulphurous acid (Böniger, Ber. 1894, 27, 3052)	*Acid sodium* salt, NaHA, sparingly soluble needles. Diazotisable in absence of mineral acid giving *diazo-oxide* (*cf.* Geigy, *l.c.* ; *v.* p. 418).
1 : 2 : 6 : 8	Reduction of azo-derivatives of β-naphthol-6 : 8-disulphonic acid (Witt, D. R.-P. 49857 ; Ber. 1888, 21, 3981).	*Acid sodium* salt, NaHA, easily soluble prisms. Gives dark brown colouration with ferric chloride. For *diazo-oxide*, *cf.* Geigy, *l.c.* ; *v.* p. 418.
1 : 4 : 3 : 6 [4 : 1 : 2 . 7]	(1) Reduction of azo-derivatives of α-naphthol-2 : 7-disulphonic acid (Reverdin and de la Harpe, Ber. 1892, 25, 1405) (2) Electrolytic reduction of α-nitronaphthalene-3 : 6-disulphonic acid (Bayer, D. R.-P. 81621).	*Acid*, sp. soluble needles ; *sodium* salt readily soluble. Gives a dark red colouration with ferric chloride (Bayer, *l.c.*). Is not diazotisable (*cf.* Reverdin and de la Harpe, Ber. 1893, 26, 1284).
1 : 4 : 3 : 7 [4 : 1 : 2 : 6]	Electrolytic reduction of α-nitronaphthalene-3 : 7-disulphonic acid (Bayer, D. R.-P. 81621).	*Barium* salt, sparingly soluble. Gives a rose-red colouration with ferric chloride.
1 : 4 : 3 : 8 [4 : 1 : 2 : 5]	Reduction of 4-nitroso-α-naphthol-2 : 5-disulphonic acid (Friedländer, Ber. 1895, 28, 1536).	*Acid*, readily soluble needles. Is not diazotisable, and does not couple with diazotised bases.
1 : 5 : 2 : 7 [5 : 1 : 3 : 6]	α-Naphthylamine-2 : 5 : 7-trisulphonic acid heated with 50 p.c. caustic potash at 180°–200° (Bayer, D. P. Anm. F. 7001 ; Eng. P. 17141B of 1893 ; Cassella, D. R.-P. 188505).	*Acid sodium* salt, moderately soluble needles. Gives wine-red colouration with ferric chloride. Forms an orange-red soluble *diazo*-compound, which with sodium carbonate solution becomes sky-blue and then orange
1 : 5 : 3 . 7 [5 : 1 : 3 : 7]	Fusion of α-naphthylamine-3 : 5 : 7-trisulphonic acid with caustic soda at 160°–170° (Cassella, D. R.-P. 75432).	*Acid* and *acid sodium* salt readily soluble (Cassella, D. R.-P. 84952). Gives dark-green coln. with ferric chloride (*ibid.*). Forms an orange *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Cassella, *l.c.* ; D. R.-P. 83011).
1 : 5 : (4) : (6) 5 : 1 : (2) : (8)	1-Amino-5-naphthol sulphonated with 23 p.c. anhydro-acid at 100° (Aktienges., D. P. Anm. A. 3767).	*Acid* and *sodium* salt readily soluble. Forms a yellow *diazo*-compound. Couples with diazotised bases
1 : 6 : 3 : 5 [5 : 2 : 1 : 7]	1-Amino-6-naphthol-3-sulphonic acid sulphonated with 12 p.c. anhydro-acid below 20° (Cassella, D. P. Anm. C. 5163 ; *cf.* D. R.-P. 84952).	*Acid sodium* salt readily, *calcium* salt sparingly sol. Gives violet-black colouration with ferric chloride. Forms a yellow soluble *diazo*-compound. Couples in acid or alkaline solution with diazotised bases, but gives only one series of *monoazo*-dyes.
1 : 6 : 3 : 7 [5 : 2 : 3 : 7]	1 - Amino - 6 - naphthol - 3 - sulphonic acid heated with sulphuric acid at 140°–150°, *or* the 3 : 5-disulphonic acid heated with sulphuric acid at 150° (Cassella, D. R.-P. 84952).	*Acid sodium* salt, sparingly soluble needles. Gives greenish-black colouration with ferric chloride. Forms a soluble *diazo*-compound Couples in alkaline solution with diazotised bases (*cf.* Cassella, *l.c.* ; D. R.-P. 95988).
1 : 7 : (4) : ? [8 : 2 : (5) : ?]	1-Amino-7-naphthol sulphonated with sulphuric acid above 100° (Cassella, D. R.-P. 69458 ; *cf.* Cassella, D. R.-P. 75066).	*Acid* readily soluble.
1 : 8 : 2 : 4 [8 : 1 : 5 : 7] **2 S-acid.**	Fusion of naphthasultam-2 : 4-disulphonic acid ('α-naphthylamine-2 : 4 : 8-trisulphonic acid') with 90 p.c. caustic soda at 170° (Aktienges., D. P. Anm. A. 3346 ; Eng. P. 2984 of 1893 ; Bayer, D. R.-P. 79566 ; 80668 ; Eng. P. 4979 of 1893 ; Cassella, D. R.-P. 75710 ; Dressel and Kothe, Ber. 1894, 27, 2141).	*Acid* readily sol. ; *acid sodium* salt, $NaHA+H_2O$, easily sol. needles ; *calcium* salt moderately sol. Gives a greenish-black coln. with ferric chloride. Forms a reddish-yellow soluble *diazo*-compound. Couples in acetic acid or in alkaline solution with diazotised bases giving only one series of *monoazo*-dyes, but in HCl solution, *disazo*-dyes of the 4-monosulphonic acid may be formed (*cf.* Bayer, D. R.-P. 77703 ; Eng. P. 4979 of 1893).
1 : 8 : (2) : (5) 8 : 1 : (4) : (7) **L-acid.**	1 : 8-Diaminonaphthalene-(2) : 5-disulphonic acid boiled with 20 p.c. sulphuric acid (Cassella, D. R.-P. 73048).	*Acid* moderately, *acid sodium* salt readily soluble. Gives brown colouration with ferric chloride. Forms yellow *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 84952).
1 : 8 : 2 : ? [8 : 1 : ? : 7]	1 : 8-Diaminonaphthalenetrisulphonic acid boiled with water or 10 p.c. sulphuric acid (Fischesser, D. P. Anm. F. 7595 ; Eng. P. 13203 of 1894).	*Acid sodium* salt, NaHA, moderately soluble. Gives green colouration with ferric chloride. Forms a soluble yellow *diazo*-compound. Couples in acid solution with diazotised bases.
1 : 8 : 3 : 5 [8 : 1 : 4 : 6] **B-acid.**	1 - Amino - 8 - naphthol - 3 - sulphonic acid sulphonated with monohydrate at the ordinary temperature (Leonhardt, D. P. Anm. F. 8626 ; Eng. P. 19253 of 1895 ; Cassella, D. R.-P. 108848).	*Acid* and *acid sodium* salt sparingly soluble. Forms a yellow sparingly soluble *diazo*-compound. Couples in acid or alkaline solution with diazotised bases, forming two series of *monoazo*-dyes (*cf.* Cassella, *l.c.*). For *aryl* derivatives, see p. 488.

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S : S		
1 : 8 : 3 : 6 [8 : 1 : 3 : 6] **H-acid.**	(1) 1 : 8-Diaminonaphthalene-3 : 6-disulphonic acid heated with 10 p.c. sulphuric acid at 100°–120°, or with 40 p.c. caustic soda at 200° (Cassella, D. R.-P. 67062; Eng. P. 1742 of 1891), *or* its azimino-derivative heated with 80 p.c. sulphuric acid at 170° (Cassella, D. R.-P. 69963) (2) Naphthasultam - 3 : 6 - disulphonic acid fused with 90 p.c. caustic soda at 170° (Bayer, D. R.-P. 80668; Eng. P. 4979 of 1893; Dressel and Kothe, Ber. 1894, 27, 2150), *or* α-naphthylamine-3 : 6 : 8-trisulphonic acid with caustic soda at 180°–190° (Bayer, D. R.-P. 69722; Eng. P. 13443 of 1890), *or* 8-chloro-α-naphthylamine-3 : 6-disulphonic acid with caustic alkali (Badische, D. R.-P. 147852) (3) 1 . 8-Dinitronaphthalene-3 . 6-disulphonic acid heated with sodium bisulphite solution at 90°–100° (Bayer, D. R.-P. 113944; Eng. P. 21138 of 1899)	*Acid*, sparingly soluble in cold water; *acid sodium* salt, $NaHA + 1\frac{1}{2}H_2O$, and *acid barium* salt, $BaH_2A_2 + 4\frac{1}{2}H_2O$, sparingly soluble needles (Dressel and Kothe, Ber. 1894, 27, 2150). Gives brownish-red colouration with ferric chloride. Forms a soluble yellow *diazo*-compound. Couples in acid or alkaline solution with diazotised bases, forming two series of *monoazo*-dyes (*cf.* Cassella, D. R.-P. 65651; Eng. P. 1742, 6972 of 1891). Largely used in the production of *azo*-dyes. For *alkyl, acetyl, aryl, nitrobenzoyl* derivatives, *v.* p. 488. For *8-chloro-α-naphthol-*3 : 6-*disulphonic acid* obtained from H-acid by the Sandmeyer reaction, *v.* p. 474.
1 : 8 : 4 : 6 [8 : 1 : 3 : 5] **K-acid.**	Fusion of α-naphthylamine-4 : 6 . 8-trisulphonic acid with 70 p.c. caustic soda under pressure at 175° (Bayer, D. R.-P. 80741; Eng. P. 17141 of 1893; Kalle, D. R.-P. 99164; Eng. P. 515 of 1894)	*Acid sodium* salt readily soluble needles (Bayer, *l.c.*). Gives yellowish-green coln. with ferric chloride. Forms a readily soluble yellow *diazo*-compound. Couples in acid or alkaline solution with diazotised bases forming two series of *monoazo*-dyes (*cf.* Kalle, *l.c.*; D. R.-P. 108266)[1] For *acetyl, aryl, nitroaryl* derivatives, *v.* p. 488.
1 : 8 : 4 : (7) [8 : 1 : (2) : 5]	1-Amino-8-naphthol-4-sulphonic acid sulphonated with 23 p.c. anhydro-acid at the ordinary temperature (Aktienges., D. P. Anm. A. 3918; Badische, D. R.-P. 125696, Eng. P. 18366 of 1900).	*Acid sodium* salt sparingly soluble needles. Gives brownish-black coln. with ferric chloride. Forms a yellowish-brown *diazo*-compound. Couples with diazotised bases (*cf.* Aktienges., *l.c.*).
1 : 8 : 5 : 7 [8 : 1 : 2 : 4]	1-Amino-8-naphthol-5-sulphonic or 7-sulphonic acid sulphonated with monohydrate at 100° (Badische, D. R.-P. 62289, Eng. P. 9676 of 1890; *cf.* Badische, D. R.-P. 82900)	*Acid* readily soluble leaflets; *acid sodium* salt readily soluble. Gives blue colouration with ferric chloride. Forms a sparingly soluble yellow *diazo*-compound. Couples with diazotised bases (*cf.* Cassella, D. R.-P. 84952)
1 : 8 : (5) : ? [8 : 1 : (4) : ?] **D-acid.**	Fusion of naphthasultamdisulphonic acid D with 90 p.c. caustic soda at 170° (Bayer, D. R.-P. 80668, Eng. P. 4979 of 1893).	*Acid sodium* salt moderately soluble needles. Gives green colouration with ferric chloride. Couples with diazotised bases.
2 : 1 : 3 : 6	Reduction of 2-nitroso-α-naphthol-3 : 6-disulphonic acid (Geigy, D. R.-P. 171024; Eng. P. 10235 of 1904).	*Acid sodium* salt easily soluble needles. Diazotisable in absence of mineral acid giving a *diazo-oxide* (*cf.* Geigy, *l.c.*; *v.* p. 418).
2 . 1 : 3 : 8	Reduction of azo-derivatives of α-naphthol-3 : 8-disulphonic acid (Bernthsen, Ber. 1890, 23, 3093)	Diazotisable in absence of mineral acid giving a *diazo-oxide* (*cf.* Geigy, *l.c.*; *v.* p. 418).
2 : 1 : 4 : 6	Reduction of azo-derivatives of α-naphthol-4 : 6-disulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1282; *cf.* Boniger, Ber. 1894, 27, 3052).	*Acid* readily soluble; *acid sodium* salt sparingly soluble needles.
2 : 1 : 4 : 7	Reduction of azo- or nitroso- derivatives of α-naphthol-4 : 7-disulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1282; *cf.* Boniger, Ber. 1894, 27, 3054).	*Acid*, moderately soluble needles; *sodium* salt readily soluble. Diazotisable in absence of mineral acid giving a *diazo-oxide* (*cf.* Geigy, *l.c.*; *v.* p. 418).
2 : 1 : 4 : 8	Reduction of azo-derivatives of α-naphthol-4 : 8-disulphonic acid (Reverdin and de la Harpe, Ber. 1893, 26, 1283).	*Acid* and *acid sodium* salt moderately soluble. Diazotisable in absence of mineral acid giving a *diazo-oxide* (*cf.* Geigy, *l.c.*; *v.* p. 418).
2 : 3 : 6 : 8 [3 : 2 : 5 : 7]	Sulphonation of 2-amino-3-naphthol-6-sulphonic acid (Aktienges., D. R.-P. 86448; Eng. P. 8645 of 1895).	No description published.
2 : 4 : 6 : 8 [8 : 1 : 5 : 7]	Digestion of β-naphthylamine-4 : 6 : 8-trisulphonic acid with 60 p.c. caustic soda at 170°–180° (Bayer, D. P. Anm. F. 8154; D. R.-P. 89242).	*Acid sodium* salt, moderately soluble Gives bluish-green colouration with ferric chloride. Forms a pale yellow *diazo*-compound. Couples with diazotised bases.
2 : 5 : 1 : 7 [6 : 1 : 3 : 5	Digestion of β-naphthylamine-1 : 5 : 7-trisulphonic acid with 66 p.c. caustic soda at 160°–220° (Bayer, D. R.-P. 80878; Eng. P. 20580 of 1893).	*Acid sodium* salt readily soluble needles. Gives green colouration with ferric chloride. Forms an orange-yellow soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Bayer, D. R.-P. 92708; Eng. P. 1062 of 1894).

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[1] The colouration produced by the interaction of K-acid with sulphanilic acid in the presence of nitrous acid forms a delicate test for minute quantities of nitrites in water (Erdmann, Ber. 1900, 33, 213).

Constitution.	Preparation.	Acids, Salts and Reactions.
N : O : S : S **2 : 5 : 3 : 7** [6 : 1 : 3 : 7]	β-Naphthylamine-3 : 5 : 7-trisulphonic acid heated with 30 p.c. caustic soda at 190° (Oehler, D. R.-P. 158147; Eng P. 1581 of 1904).	*Acid sodium* salt easily soluble. Gives yellowish-brown coln. with ferric chloride. Forms an easily soluble orange *diazo*-compound. Couples in alkaline solution with diazotised bases.
2 : 7 : 3 : 6 [7 : 2 : 3 : 6]	(1) β-Naphthylamine-3 : 6 : 7-trisulphonic acid heated with 55 p c. caustic soda at 180°–240° (Bayer, D P. Anm. F. 7019; Eng P 17141 of 1893; *cf* Bayer, D R -P. 80878) (2) 2 . 7-Dihydroxynaphthalene-3 . 6-disulphonic acid heated with 23 p c ammonia at 180°–220° (Aktienges., D. R -P. 75142, Eng. P 16199 of 1893) (3) 2-Amino-7-naphthol sulphonated with sulphuric acid at 30° (Cassella, D. R.-P. 131526).	*Acid* sparingly soluble; *acid sodium* salt sparingly soluble needles. Gives deep violet colouration with ferric chloride (Bayer, *l c* ; Aktienges., *l.c*). Forms a sparingly soluble yellow *diazo*-compound (Cassella, *l c*) Couples only slowly or not at all with diazotised bases (Cassella, *l.c.*).
2 : 8 : 3 : 6 [7 : 1 : 3 : 6] **R-acid.**	Fusion of β-naphthylamine-3 : 6 : 8-trisulphonic acid with 80 p c. caustic soda at 220°–260° (Hoeist, D. R.-P 53023; Eng P. 15175 of 1889).	*Acid* and *salts* readily soluble. Gives dark green colouration with ferric chloride. Forms a yellow sparingly soluble *diazo*-compound. Couples in alkaline solution with diazotised bases (*cf.* Aktienges., D. R.-P. 108215; Eng. P. 14895 of 1893).

Aminonaphtholtrisulphonic Acids.

1-Amino-2-naphthol- and 2-amino-1-naphthol-3 : 6 : 8-trisulphonic acids are obtained by reduction of azo-derivatives of the corresponding β-naphthol- and α-naphthol-3 . 6 : 8-trisulphonic acids. They give *diazo-oxides* on diazotisation in absence of mineral acid (Geigy, D. R.-P. 171024; Eng P. 10235 of 1904; *v* p. 418).

1-Amino-8-naphthol-2 : 4 : 6-trisulphonic acid, obtained by fusing naphthasultam-2 : 4 : 6-trisulphonic acid with 85 p c caustic potash at 150°–160°, forms a sparingly soluble *acid potassium* salt, gives a green colouration with ferric chloride, also a readily soluble orange *diazo*-compound, and couples with diazotised bases (Bayer, D. R.-P. 84597).

NITROAMINONAPHTHOLSULPHONIC ACIDS.

Nitroamino-1-naphthol, obtained from 2 : 4-dinitro-α-naphthol by reduction with ammonium sulphide, forms yellow needles, m.p. 130° (Ebell, Ber. 1875, 8, 564).

(i.) **Nitro-1-amino-2-naphthol-4-sulphonic acid.** If nitrosulphuric acid containing sufficient dissolved anhydride to remove water formed in the reaction be added to a suspension of 1-amino-2-naphthol-4-sulphonic acid in monohydrate at 0°, nitration instead of oxidation occurs. The *nitro*-compound, yellowish-brown needles, yields a *diamino-2-naphthol-4-sulphonic acid* on reduction, and when diazotised a *diazo-oxide* closely resembling the nitro-1-diazo-2-naphthol-4-sulphonic acid of D. R.-P. 164655 in properties (Kalle, D. R.-P. 249724).

(ii.) 3-**Nitro-1-amino-4-naphthol-6-sulphonic acid** [2 : 4 : 1 : 7] obtained from naphthol yellow S by reduction with stannous chloride and hydrochloric acid (Lauterbach, Ber. 1881, 14, 2029; Finger, J. pr. Chem. 1909, [ii.] 79, 442) forms sparingly soluble golden-yellow scales and is diazotisable (Gesellsch., D. R.-P. 1[illegible]513; Eng. P. 7535 of 1906). When boiled with alcohol and copper powder, it is converted into *copper 2-nitro-α-naphthol-7-sulphonate* (Finger, *l.c.*).

(iii.) 4-**Nitro-2-amino-1-naphthol-7-sulphonic acid,** obtained when naphthol yellow S in ammoniacal solution is reduced by sodium sulphide at 90°–95°, forms yellow crystals, sparingly soluble in cold water, and can be diazotised (Gesellsch., *l.c.*).

(iv.) (8)-**Nitro-2-amino-3-naphthol-6-sulphonic acid** [(5) : 3 : 2 : 7] can be prepared by adding nitre to a solution of 2-amino-3-naphthol-6-sulphonic acid in sulphuric acid at 5°. It forms yellow needles, its *potassium* and *sodium* salts are easily soluble, and it can be diazotised (Cassella, D. R.-P. 110369; 111933).

Nitrodiazonaphtholsulphonic acids. Although in certain cases nitro-1-amino-2-naphthol- or nitro-2-amino-1-naphthol-sulphonic acids have not been described, the corresponding diazo-compounds can be obtained by nitrating *o*-diazonaphtholsulphonic acids. Nitro-1-diazo-2-naphthol-4-sulphonic acid (Geigy, D. R.-P. 164655; Eng. P. 15418 of 1904) forms pale yellow crystals, and couples with phenols and amines forming *azo*-dyes (Geigy, D. R.-P. 169683; Eng. P. 15982 of 1904). Nitro-1-diazo-2-naphthol-6-sulphonic and nitro-2-diazo-1-naphthol-5-sulphonic acids give *azo*-dyes, in which, with alkaline reducing agents, the NO_2 radicle can be converted into a diazotisable NH_2 group (Kalle, D. R.-P. 176619).

DIAMINONAPHTHOLS.

Introductory.—The diaminonaphthols have been isolated only in three cases, being very rapidly oxidised on exposure of their solutions to the air. In the table a summary is given of the hydrochlorides, obtained chiefly by reduction processes; the acetyl derivatives, by which the diaminonaphthols have been characterised; and the sulphonic acids belonging to this group of compounds:

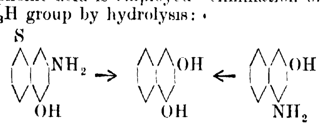
$NH_2 : NH_2 : OH$	
1 : 2 : 3 [3 : 4 : 2]	Unknown. 6-Sulphonic acid obtained by reduction of azo-dye from 2-amino-3-naphthol-6-sulphonic acid (Cassella, D. R.-P. 233939; Eng. P. 15646 of 1910).
1 : 2 : 4 [3 : 4 : 1]	Unknown. *Diacetyl methyl ether*, m.p. 254° (Henriques, Ber. 1892, 25, 3067); ***ethenyl*** **derivative, needles, m.p. 179° (Heermann, J. pr. Chem. 1892, [ii.] 45, 552).**

NH_2 : NH_2 : OH	
1 : 2 : 5 [5 : 6 : 1]	Unknown. 7-Sulphonic acid obtained by reduction of azo-dye formed by coupling diazotised *p*-nitraniline with 2-amino-5-naphthol-7-sulphonic acid in acid solution (Bayer, D. R.-P. 172319; Eng. P. 1675 of 1905).
1 : 2 : 7 [7 : 8 : 2]	Not described. Obtained by reduction of 7-hydroxy-[β-]naphthaquinonedioxime. *Hydrochloride*, B·2HCl; *triacetyl* derivative, m.p. 244°–245° (Nietzki and Knapp, Ber. 1897, 30, 1124).
1 : 2 : 8 [7 : 8 : 1]	Not isolated. Obtained by reduction of sulphonanilazo-2-amino-8-naphthol (Badische, D. R.-P. 90212; Eng P. 15953 of 1896). The 4-, 5-, 6- mono-, and 3 : 6- and 5 : 7- disulphonic acids have been obtained from the corresponding 2-amino-8-naphtholsulphonic acids (*cf.* Badische, *l.c.*), and the 6-monosulphonic acid from 2-amino-8-naphthol-6-sulphonic acid (Bayer, D R.-P. 87900; Eng. P. 6035 of 1893) by reducing the azo-dyes formed by coupling with diazotised bases.
1 : 3 : 4 [2 : 4 : 1]	Not isolated. Obtained by reduction of 2 · 4-dinitro-α-naphthol with tin and hydrochloric acid. *Hydrochloride*, B·2HCl, scales, and *sulphate*, B H_2SO_4 + $2H_2O$, needles, are both rapidly oxidised in air to *diimino-α-naphthol* (Graebe and Ludwig, Annalen, 1870, 154, 312); *triacetyl* derivative, needles, m p 280°, decomp (Meerson, Ber. 1888, 21, 1196) The 7-sulphonic acid, obtained by reduction of naphthol yellow S, gives *hydrochloride*, B HCl, in needles (Gaess, Ber. 1899, 32, 232, *cf* Lauterbach, Ber. 1881, 14, 2028), is not diazotisable, does not couple (*cf.* Aktienges, D R-P 86448; Eng. P. 8645 of 1895), and is readily oxidised to the *diimino*-compound (Lauterbach, *l c*, Gaess, *l.c.*).
1 : 3 : 5 [5 : 7 : 1]	Unknown. The 7-sulphonic acid, obtained by digesting 1 : 3-diaminonaphthalene-5 : 7-disulphonic acid with 60 p c caustic soda solution at 210°, couples with diazotised bases (Kalle, D. R-P. 92239)
1 : 3 : 8 [6 : 8 : 1]	Unknown. The 6-sulphonic acid, obtained similarly from 1 . 3-diaminonaphthalene-6 : 8-disulphonic acid, couples with diazotised bases (Kalle, D R-P. 92239).
1 : 4 : 2	Not isolated. Obtained by reduction of diacetyl-4-nitro-1-amino-2-naphthol, *or* of azo-derivatives of 1-amino-2-naphthol is rapidly oxidised to blue *oxazine* in the air (Nietzki and Becker, Ber 1907, 40, 3397; *cf* Kalle, D R-P. 195901). *Hydrochloride*, B·2HCl, needles; N-*diacetyl* derivative, m.p 250°–260°, decomp. (Kehrmann and Hertz, Ber. 1896, 29, 1417) The 6-sulphonic acid, obtained by reduction of azo-derivative of 1-amino-2-naphthol-6-sulphonic acid, forms *hydrochloride*, B HCl (Nietzki and Becker, *l c*; Kalle, *l.c.*). The 8-sulphonic acid, obtained by reduction of crocein yellow, forms *hydrochloride*, B HCl needles, readily oxidised to the *diimino*-derivative, and is diazotisable (Nietzki and Zubelen, Ber 1889, 22, 455).
1 : 4 : 8 [5 . 8 : 1]	Not described. Obtained by reduction of acetyl-4-nitro-1-amino-8-naphthol (Fichter and Gageur. Ber 1906, 39, 3336).
1 : 5 : 3 [4 : 8 : 2]	Unknown. The 7-sulphonic acid, obtained by fusing 1 · 5-diaminonaphthalene-3 : 7-disulphonic acid with 90 p c. caustic soda solution at 200°–240° forms needles sparingly soluble in hot water and couples with diazotised bases (Cassella, D. R-P 91000).
1 : 5 : 8 [4 : 8 : 1]	Not isolated. Obtained by reduction of 8-nitro-4-nitroso-α-naphthol (Friedländer and Scherzer, *cf* J Soc. Chem. Ind 1900, 19, 339, Graebe and Oeser, Annalen, 1904, 335, 155); *or* of azo-derivatives of 1-amino-8-naphthol (Fichter and Gageur, Ber. 1906, 39, 3333). *Hydrochloride*, B 2HCl; *N-diacetyl* derivative, needles, m p 247°, *triacetyl* derivative, m.p. 258° (Fichter and Gageur, *l c*)
1 : 6 : 2	M.p 194° (*cf.* Cassella, D. R-P. 117298; Eng. P. 16149 of 1899) Obtained by reduction of 1 : 6-dinitro-β-naphthol (Loewe, Ber 1890, 23, 2543; Kehrmann and Matis, Ber. 1898, 31, 2413). *Hydrochloride*, B 2HCl, needles; N-*diacetyl* derivative, needles, m.p. 235°; *triacetyl* derivative, needles, m p. 203° (Loewe, *l c*).
1 : 7 : 2	Scales, m p 220° (decomp.). Obtained by reduction of azo- derivative of 7-amino-2-naphthol (Cassella, D. R-P. 117298, Eng P. 16149 of 1899). *Sulphate*, sparingly soluble (*ibid.*); N-*diacetyl* derivative, needles, m.p. 226°; *triacetyl* derivative, needles (Kehrmann and Wolff, Ber. 1900, 33, 1540).
1 : (?) : 2	Unknown. The 4-sulphonic acid, obtained by reduction of nitro-1-amino-2-naphthol-4-sulphonic acid, gives *hydrochloride* in needles (Kalle, D R.-P. 249724).
1 : 7 : 8 [2 8 : 1]	Not isolated. Obtained by reduction of 1-amino-7-nitroso-8-naphthol. *Hydrochloride*, B·2HCl, needles; *triacetyl* derivative, needles, m.p. 234° (Fichter and Gageur, Ber. 1906, 39, 3338). The 3 · 6-disulphonic acid, obtained by reduction of azo- derivative of 1-amino-8-naphthol-3 : 6-disulphonic acid, is not diazotisable in acid solution (Hochst, D. R.-P. 92012). The 4-mono- and 4 : 6-di-sulphonic acids, obtained similarly from azo-derivatives of 1-amino-8-naphthol-4-mono- and 4 : 6-di-sulphonic acids, have been introduced like the 3 : 6-disulphonic acid, as photographic developers (Schultz, D. R.-P. 101953).
1 : 8 : 4 [4 : 5 : 1]	Not isolated Obtained by reduction of 5-nitro-4-nitroso-α-naphthol (Friedländer and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339; Graebe and Oeser, Annalen, 1904, 335, 152). *Hydrochloride*, B 2HCl.
2 : 3 : 8 [6 7 : 1]	Unknown. The 6-sulphonic acid, obtained by digesting 2 . 3-diaminonaphthalene-6 : 8-disulphonic acid with 90 p.c. caustic potash solution at 190°–200°, forms an *azimino*-derivative with nitrous acid, and couples with diazotised bases (Aktienges., D. R-P. 86448; Eng. P. 8645 of 1895).
2 : 6 : 1	Not isolated. Obtained by reduction of 6-nitronaphthalene-2-diazo-1-oxide. *Hydrochloride*, not described; *triacetyl* derivative, needles, m.p. 261°, decomp. (Gaess and Ammelburg, Ber. 1894, 27, 2213).
2 : 7 : 8 [2 : 7 : 1]	Unknown. The 6-sulphonic acid, obtained by reduction of azo- derivative of β-naphthylamine-6 : 8-disulphonic acid, is not diazotisable in acid solution (Höchst, D. R.-P. 92012).

VIII. DIHYDROXY- DERIVATIVES.

Introductory.—The dihydroxynaphthalenes, like the naphthols, can be obtained from naphthalenesulphonic acids by fusion with caustic alkali. For this purpose the four disulphonic acids producible from naphthalene by sulphonation, six of the naphtholmonosulphonic acids and β-naphthol-3 : 6-disulphonic acid have been employed. It has not been possible to prepare 1 : 2-, 1 : 3- or 1 : 4-dihydroxynaphthalene by this method.

Another process, although less general, in which diaminonaphthalenes, aminonaphthols or aminonaphtholsulphonic acids are heated with dilute mineral acid under pressure, leads to the formation of dihydroxynaphthalenes by exchange of the NH_2 radicle for OH, and—when a sulphonic acid is employed—elimination of the SO_3H group by hydrolysis:



The conversion of certain of the diaminonaphthalenes and aminonaphthols into dihydroxynaphthalenes may also be effected by the bisulphite method (*v.* p. 416).

For the preparation of the 1 : 2- and 1 : 4-dihydroxynaphthalenes (naphthaquinols), reduction of the respective naphthaquinones is the only practicable method.

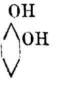
The dihydroxynaphthalenes, of which the complete series of ten is known, are easily soluble in caustic alkali solutions, but only sparingly so in cold water; the alkaline solutions rapidly become dark brown or black on exposure to the air.

When heated with ammonia under pressure, the four αβ-dihydroxynaphthalenes yield β-amino-α-naphthols as intermediate products, thus resembling β- rather than α-naphthol.

With nitrous acid the heteronuclear dihydroxynaphthalenes yield mononitroso- compounds, which, when the nitroso- group occupies the *ortho-* position, furnish lakes with chromium or iron salts. The nitroso- derivative formed from the monoalkyl ether of 1 : 8-dihydroxynaphthalene is said closely to resemble 2-nitroso-α-naphthol, and that from the 2 : 6- or 2 : 7-dihydroxy- derivative 1-nitroso-β-naphthol in properties.

Most of the dihydroxynaphthalenes by coupling with diazotised bases furnish monoazo-dyes which form lakes with chromium or iron salts. Fastness on chromed wool is a distinguishing feature of the *ortho*-monoazo- dyes produced by coupling the 1 : 5-, 1 : 7- and 2 : 6-isomerides respectively in weak alkaline solution with diazotised *o*-aminophenolsulphonic acids (Bayer, D. R.-P. 157786; 164318; 164317; Eng. P. 18569 of 1902; *v.* p. 507). Azo- dyes obtained by coupling 1 : 3-dihydroxynaphthalene have a characteristic yellow shade.

DIHYDROXYNAPHTHALENES.



(i.) 1 : 2-**Dihydroxynaphthalene** ([β-]*naphthaquinol*, [β-]*naphthahydroquinone*) is obtained by reducing [β-]naphthaquinone with sulphurous acid in the cold (Liebermann and Jacobson, Annalen, 1882, 211, 58; Paul, Z. angew. Chem. 1897, 10, 24); *or* by heating 1-amino-2-naphthol-6 : 8-disulphonic acid with water under pressure above 200° (Bayer, D. R.-P. 89242).

Identification.—It forms scales, m.p. 60°, dissolves in alkalis forming yellow solutions which become green on exposure to the air, and in aqueous solution exerts a severe caustic action on the skin (Liebermann and Jacobson, *l.c.*; Paul, *l.c.*). The *diacetate* forms scales, m.p. 110° (Crépieux, Bull. Soc. chim. 1891, [iii.] 5, 158); the 1-*methyl ether*, monoclinic plates, m.p. 90·5°; the *dimethyl ether*, m.p. 31°, b.p. 278°–280° (Bezdzik and Friedlander, Monatsh. 1909, 30, 280).

Reactions.—With diazotised bases it couples, forming *azo-* dyes which give red to bluish-violet lakes with aluminium or chromium salts (Witt, D. R.-P. 49979; Eng. P. 2499 of 1889; *cf.* Paul, *l.c.*). In aqueous solution with ferric chloride, it yields [β-]*naphthaquinone* (Zincke, Annalen, 1892, 268, 275). Nitric acid of sp.gr. 1·48 converts it into 3-*nitro*-[β-]*naphthaquinone* (Korn, Ber. 1884, 17, 3024; *cf.* Zincke, *l.c.*).

(ii.) 1 : 3-**Dihydroxynaphthalene** is obtained when 1-amino-3-naphthol is boiled with dilute acid (Friedlander, Ber. 1895, 28, 1952); *or* when 1-amino-3-naphthol-4-sulphonic acid is heated with water or dilute acid at 120° (Friedlander and Rudt, Ber. 1896, 29, 1609); *or* when 2-amino-4-naphthol-8-sulphonic acid (Bayer, D. R.-P. 87429; D. P. Anm. F. 8070; Eng. P. 3580 of 1895), or 1 : 3-dihydroxynaphthalene-7-mono- or 5 : 7-disulphonic acid (Bayer, D. R.-P. 90096; Eng. P. 4962 of 1895) is heated with 5 p.c. sulphuric acid at 235°; *or* when 1 : 3-dihydroxy-β-naphthoic acid is heated with water at 100° (Metzner, Annalen, 1897, 298, 388).

Identification.—It crystallises from water in scales, m.p. 124°, is almost insoluble in benzene, becomes rapidly brown in alkaline solution on exposure to the air, and gives with ferric chloride a yellowish-brown precipitate. The *diacetate* forms prisms, m.p. 56° (Friedländer and Rüdt, *l.c.*).

Reactions.—With diazotised bases it couples in alkaline or weak acid solution, giving *azo-* dyes characterised by their yellow colour (Friedländer and Rüdt, *l.c.*). Digestion with 60 p.c. caustic soda solution at 180°–200° converts it into *o-toluic acid* (Friedländer and Rüdt, *l.c.*; Kalle, D. R.-P. 79028). When heated with aqueous ammonia at 130°–140°, it yields 2-*amino-4-naphthol* or 1 : 3-*diaminonaphthalene*, and with aniline *phenyl-2-amino-4-naphthol*. Condensed with phthalic anhydride and either phosphoric oxide at 130°, or zinc chloride at 200°, it furnishes *naphthafluorescein* (Friedländer and Rudt, *l.c.*; Bayer, D. R.-P. 84990; Eng. P. 3497 of 1895).

(iii.) 1 : 4-**Dihydroxynaphthalene** ([α-]*naphthaquinol*, [α-]*naphthahydroquinone*) is formed when [α-]naphthaquinone is reduced with hydriodic acid and phosphorus (Groves, Chem. Soc. J. 1873, 26, 210); with tin and hydrochloric acid, or at 140°–150° with sulphurous acid (Plimpton, Chem. Soc. Trans. 1880, 37, 635); or with stannous chloride and very dilute hydrochloric acid (Russig, J. pr. Chem. 1900, [ii.] 62, 32). It is best prepared by adding powdered [α-]

naphthaquinone to a boiling mixture of tin and hydrochloric acid.

Identification.—It crystallises in needles, m.p. 176°, and is readily soluble in alcohol, ether, or boiling water, but only sparingly so in benzene. By chromic acid or other oxidising agents, it is converted into [α-]*naphthaquinone*. The *diacetate* forms tablets, m.p. 128°–130° (Korn, Ber. 1884, 17, 3025).

Alkyl derivatives. The *monomethyl ether*, obtained by etherification at the ordinary temperature with 18 p.c. methyl alcoholic hydrogen chloride, forms needles, m.p. 131°; the *monoethyl ether*, prepared by boiling the dihydroxynaphthalene with 3 p.c. ethyl alcoholic hydrogen chloride, forms needles, m.p. 105° (Badische, D. R.-P. 173730; Eng. P. 7287A of 1906; *cf.* Russig, J. pr. Chem. 1900, [ii.] 62, 50). These ethers, which can also be obtained by heating 1-amino-4-naphthol hydrochloride with the respective alcohol under pressure at 170°–180° (Hochst, D. R.-P. 234411), when coupled with diazotised aminosulphonic acids, furnish *ortho*-azo- dyes (Badische, D. R.-P. 176640; Eng. P. 7287 of 1906). The *dimethyl* ether forms needles, m.p. 85° (Russig, *l.c.*).

(iv.) 1 : 5-**Dihydroxynaphthalene** is formed when potassium α-naphthol-5-sulphonate is fused with caustic potash at 200°–250° (Cleve, Bull. Soc. chim. 1875, [ii.] 24, 513; Erdmann, Annalen, 1888, 247, 356; *cf.* Ewer and Pick, D. R.-P. 41934); *or* when sodium naphthalene-1 : 5-disulphonate is fused with caustic soda at 220°–260° (Ewer and Pick, *l.c.*; Bernthsen and Semper, Ber. 1887, 20, 938; Schultz, *ibid.* 3161); *or* when 1 : 5-diaminonaphthalene or 1-amino-5-naphthol is either heated with 4 p.c. hydrochloric acid under pressure at 180° (Aktienges., D. P. Anm. A. 4029), or boiled with sodium bisulphite solution and the product decomposed by alkali (Bucherer, J. pr. Chem. 1904, [ii.] 69, 84; *cf.* 70, 352).

Identification.—It crystallises from water in scales, m.p. 265° (Bentley, Robinson and Weizmann, Chem. Soc. Trans. 1907, 91, 106), sublimes in needles, is almost insoluble in benzene, reduces silver solution, and in alkaline solution becomes dark brown on exposure to the air—a property which has suggested its use as a hair-dye (Erdmann, D. R.-P. 51073). The *diacetate* forms feathery crystals, m.p. 159°–160° (Bernthsen and Semper, *l.c.*); the *dibenzoate*, scales, m.p. 235° (Fischer, J. pr. Chem. 1916, [ii.] 94, 14); the *monomethyl ether*, leaflets, m.p. 140°; and the *dimethyl ether*, needles, m.p. 183°–184° (Bentley, Robinson and Weizmann, *l.c.*).

Reactions.—It couples with most diazotised bases forming para-*azo*- dyes (Fischer and Bauer, J. pr. Chem. 1917, [ii.] 95, 265; *cf.* Erdmann, Annalen, 1888, 247, 356), or *disazo*- dyes if the coupling be effected in alkaline solution (Badische, D. P. Anm. B. 33987; Eng. P. 10536 of 1903). With nitrous acid, it gives the 2-*nitroso*- derivative (Fischer, *l.c.*; *cf.* Read, Holliday & Co., D. R.-P. 68809; Eng. P. 1812 of 1890). On oxidation with chromic acid mixture, it is converted into *juglone* (5-hydroxy-[α-]naphthaquinone; *cf.* Bernthsen and Semper, *l.c.*). Sulphuric acid at 50°–60° converts it into a mixture of the 2- and 4-*monosulphonic acids*, but at 100°–160° into a *disulphonic acid*. By digestion with ammonia at 250°–300° or by the bisulphite reaction, it yields 1 : 5-*diaminonaphthalene*. When heated with potassium hydrogen carbonate suspended in anhydrous media at 230°, a *dicarboxylic acid*, m.p. 300°, is obtained (Hemmelmayr, Monatsh, 1917, 38, 84; D. R.-P. 296035; 296501).

(v.) 1 : 6-**Dihydroxynaphthalene** is formed when sodium naphthalene-1 : 6-disulphonate is fused with caustic soda at 230°–250° (Ewer and Pick, D. R.-P. 45229); *or* when β-naphthol-5-sulphonic acid is fused with caustic potash and a little water at 260° (Claus, J. pr. Chem. 1889, [ii.] 39, 316); *or* when 1 : 6-dihydroxynaphthalene-4-sulphonic acid is desulphonated by sodium amalgam (Friedlander and Lucht, Ber. 1893, 26, 3034).

Identification.—It crystallises from benzene in small prisms or serrated scales, m.p. 135°, sublimes in scales, is only sparingly soluble in water, and with ferric chloride gives a transient blue colouration. The *diacetate* forms prisms, m.p. 73° (Claus, *l.c.*); the *dibenzoate*, prisms, m.p. 103°–104°; the *dimethyl ether*, needles, m.p. 60°–61°; and the *diethyl ether*, needles, m.p. 83° (Fischer and Bauer, J. pr. Chem. 1916, [ii.] 94, 2).

Reactions.—It couples in acid solution with diazotised bases forming *monoazo*- dyes almost entirely of the para- type or in alkaline solution giving *disazo*- dyes (Fischer and Bauer, *l.c.*). With nitrous acid it yields chiefly the 2-*nitroso*- mixed with some of the 4-*nitroso*- derivative (Fischer and Bauer, *l.c.*; *cf.* Read, Holliday & Co., D. R.-P. 68809; Eng. P. 1812 of 1890). Digestion with ammonia at 150°–300° converts it into 1 : 6-*diaminonaphthalene*. When heated with a mixture of potassium carbonate and bicarbonate in an anhydrous medium, it furnishes a *monocarboxylic acid*, m.p. 200° (Hemmelmayr, Monatsh. 1917, 38, 86). Heated with an equal weight of phthalic anhydride at 180°–200°, it gives 3 : 11-*dihydroxynaphthafluoran*, which forms oxonium salts with acids (Fischer and Konig, Ber. 1914, 47, 1076; 1917, 50, 1011; Hochst, D. R.-P. 275897; *cf.* Konig, Chem. Zeit. 1914, 38, 483), but if boric acid be present 1 : 6-*dihydroxynaphthoyl-o-benzoic acid* is the product, which is sweet enough to be a sugar substitute (Gesellsch., D. R.-P. 311213).

(vi.) 1 : 7-**Dihydroxynaphthalene** is obtained by fusing β-naphthol-8-sulphonic acid with caustic potash (Emmert, Annalen, 1887, 241, 371; Bayer, D. R.-P. 53915; Eng. P. 14230 of 1889); *or* by heating 1 : 7-dihydroxynaphthalene-3-sulphonic acid with dilute mineral acid (*cf.* Bayer, D. R.-P. 85241); *or* by boiling 1 : 7-dihydroxy-β-naphthoic acid with aniline to eliminate carbon dioxide (Friedländer and Zinberg, Ber. 1896, 29, 40).

Identification.—It crystallises in needles, m.p. 178°, is moderately soluble in water, but readily so in benzene, rapidly becomes black on exposure in alkaline solution to the air, and with ferric chloride gives at first (like α-naphthol) a white turbidity which with more of the reagent becomes blue (Friedländer and Zinberg, *l.c.*). The *diacetate* forms rhombic tables, m.p. 108° (Emmert, *l.c.*).

Reactions.—It couples in alkaline solution with diazotised *o*-aminophenolsulphonic acids furnishing *monoazo*- dyes (Bayer, D. R.-P. 164318; Eng. P. 18569 of 1902). With nitrous acid it yields a *mononitroso*- derivative (Bayer,

D. R.-P. 53915). Heated, as sodium derivative, with carbon dioxide under pressure at 140°, it gives 1 : 7-*dihydroxy-β-naphthoic acid* (Heyden, D. R.-P. 55414).

(vii.) 1 : 8-**Dihydroxynaphthalene** is obtained when either naphthasultone or α-naphthol-8-sulphonic acid is fused with 75 p.c. caustic potash solution at 220°–230° (Erdmann, Annalen, 1888, 247, 356); *or* when α-naphthylamine-8-sulphonic acid is heated with 9 p.c. caustic soda solution under pressure at 220°–260° (Höchst, D. P. Anm. F. 6311). It is also formed when 1 : 8 - dihydroxynaphthalene - 4 - sulphonic acid (Bayer, D. R.-P. 67829; Eng. P. 13565 of 1889; *cf.* Heller and Kretzschmann, Ber. 1921, 54, 1098), *or* 1 : 8-dihydroxynaphthalene-2 : 4-disulphonic acid (Dressel and Kothe, Ber. 1894, 27, 2143), *or* naphthasultamdisulphonic acid D (Bayer, D. R.-P. 80668; Eng. P. 4979 of 1893) is heated with 20 p.c. sulphuric acid at 160°-200°; *or* when 1 : 8-diaminonaphthalene is heated with 17 p.c. hydrochloric acid under pressure at 180° (Aktienges., D. P. Anm. A. 4028).

Identification.—It crystallises in long needles, m.p. 140°, or with 1 mol. H_2O in scales, oxidises rapidly when moist on exposure to the air, is only sparingly soluble in water but dissolves readily in benzene, and gives with ferric chloride a white flocculent precipitate, which rapidly becomes green. The *diacetate* forms scales, m.p. 147°–148° (Erdmann, *l.c.*)

Reactions.—With diazotised bases, it couples in acid solution giving 4-*monoazo-* dyes (Badische, D. R.-P. 51559), but in alkaline or acetic acid solution 4 : 7-*disazo-* dyes (Friedlander and Silberstern, Monatsh. 1902, 23, 518; Heller and Kretzschmann, *l.c.*). With nitrous acid it furnishes a *mononitroso-* derivative (Heller and Kretzschmann, *l.c.*; *cf.* Bayer, D. R.-P. 51478; Eng. P. 14230 of 1889). On oxidation with chromic acid mixture, it yields 5-*hydroxy-*[α-]*naphthaquinone* in small quantity (Erdmann, *l.c.*). Heated, as sodium derivative, with carbon dioxide under pressure at 140°, it yields 1 : 8-*dihydroxy-β-naphthoic acid* (Heyden, D. R.-P. 55414). When warmed with sulphuric acid at 50°, it is converted into a mixture of the I-, G-, and R-*disulphonic acids* (Badische, D. R.-P. 79029, 79030; *cf.* Eng. P. 14294 of 1891).

By condensation with acyl chlorides or anhydrides in presence of zinc chloride at 140°–150°, yellow or orange dihydroxyketones (*e.g.* 1 : 8-*dihydroxy-2-acetonaphthone*, needles, m.p. 100°–101°, and *benzonaphthone*, needles, m.p. 121°-122°) are obtained which form lakes with alumina, &c. (Lange, D. R.-P. 126199; Eng. P. [illegible]970 of 1900; *cf.* D. R.-P. 129035, 129036).

(viii.) 2 : 3-**Dihydroxynaphthalene** has been prepared by fusing β-naphthol-3 : 6-disulphonic acid, or 2 : 3-dihydroxynaphthalene-6-sulphonic acid, with 90 p.c. caustic soda solution at 280°–320° (Badische, D. R.-P. 57525; Eng. P. 15803 of 1890); also by heating 2 : 3-dihydroxynaphthalene-6-sulphonic acid with 25 p.c. sulphuric acid at 200° (*ibid.*; Friedländer and Zakrzewski, Ber. 1894, 27, 762); *or* 2-amino-3-naphthol-6-sulphonic acid with dilute mineral acid under pressure at 180°–200° (Höchst, D. R.-P. 73076; *cf.* Friedländer and Zakrzewski, *l.c.*).

Identification.—It forms monoclinic scales (Siegmund, Monatsh. 1908, 29, 1087), m.p. 160°–161°, is sparingly soluble in water, and gives with ferric chloride a dark blue colouration or precipitate (Badische, *l.c.*). The *monomethyl ether* forms needles, m.p. 108°; *dimethyl ether*, needles, m.p. 115°–116°; *monoethyl ether*, m.p. 109°–110°; *diethyl ether*, m.p. 96°–97° (Friedländer and Silberstern, Monatsh. 1902, 23, 519; Silberstern, D. R.-P. 133459).

Reactions.—With diazotised bases it couples giving in an acetic acid bath 1-*monoazo-* dyes, and in an alkaline bath 1 : 4-*disazo-* dyes (Friedlander and Silberstern, *l.c.*; *cf.* Friedländer and Zakrzewski, *l.c.*; Badische, D. R.-P. 62947). By the bisulphite method at 80° or when digested with 30 p.c. ammonia at 140°–150° it yields 2-*amino-3-naphthol*, but at 250°, 2 : 3-*diaminonaphthalene.*

(ix.) 2 : 6-**Dihydroxynaphthalene** is obtained by fusing sodium naphthalene-2 . 6-disulphonate (*cf.* Armstrong and Graham, Chem. Soc. Trans. 1881, 39, 140), *or* sodium β-naphthol-6-sulphonate (Armstrong and Graham, *l.c.*; Emmert, Annalen, 1887, 241, 369) with caustic potash.

Identification.—It forms rhomb-like scales, m.p. 218° (Willstatter and Parnas, Ber. 1907, 40, 1410), dissolves only sparingly in water (1 litre at 14° dissolves 1·08 grm.) or light petroleum, shows strong blue fluorescence in alkaline solution, gives with ferric chloride a yellowish-white precipitate, and has a strong caustic effect on the skin. The *diacetate* forms scales, m.p. 175° (Emmert, *l.c.*); the *dimethyl ether*, rhomb-like scales, m.p. 150° (Willstatter and Parnas, *l.c.*); the *diethyl ether* scales, m.p. 162° (Emmert, *l.c.*).

Reactions.—It couples furnishing in acetic acid solution 1-*monoazo-*dyes (Kehrmann, Ber. 1907, 40, 1962) or in alkaline solution 1-*monoazo-* mixed with *disazo-* dyes (Kaufler and Brauer, Ber. 1907, 40, 3276). With nitrous acid it gives the 1-*nitroso-* derivative (Bayer, D. R.-P. 55126, 59268; Eng. P. 14230 of 1889). In boiling benzene solution it is oxidised by lead peroxide to 2 : 6-*naphthaquinone.* Heated with ammonia at 150°–300°, it yields 2 : 6-*diaminonaphthalene*, and with aniline at 170°, *diphenyl-2 : 6-diaminonaphthalene.* Monohydrate at 5° converts it into an acid which Bayer & Co. consider to be the 4-monosulphonic acid (D. R.-P. 72222), but Jacchia, the 1 : 5-*disulphonic acid* (Annalen, 1902, 323, 114); with sulphuric acid at 100° it gives a *disulphonic acid* (Griess, Ber. 1880, 13, 1959).

(x.) 2 : 7-**Dihydroxynaphthalene** is formed when sodium naphthalene-2 : 7-disulphonate is fused with caustic soda at 290°–300° (Ebert and Merz, Ber. 1876, 9, 609; Weber, Ber. 1881, 14, 2206); *or* when β-naphthol-7 sulphonic acid is fused with caustic soda (Pfitzinger and Duisberg, Ber. 1889, 22, 398). It is also formed when 2 : 7 - dihydroxynaphthalene - 3 : 6 - disulphonic acid is heated with 20 p.c. sulphuric acid at 200° (Bayer, D. P. Anm. F. 7243; Eng. P. 25074A of 1893).

Identification.—It forms needles, m.p. 190° (Clausius, Ber. 1890, 23, 520), dissolves readily in hot water, but only sparingly so in benzene, and gives no colouration with ferric chloride, but blackens rapidly in alkaline solution. The *diacetate* forms scales, m.p. 136° (Clausius, *l.c.*); the *dibenzoate*, scales, m.p. 138°–139° (Weber, *l.c.*); the *monomethyl ether*, needles, m.p. 117°, its *acetate* needles m.p. 130°, and its *nitroso-*compound, scales, m.p. 129° (Fischer and

Hammerschmidt, J. pr. Chem. 1916, [ii.] 94, 24); the *dimethyl ether*, tablets, m.p. 138° (Fischer and Kern, *ibid.* 34) and the *diethyl ether*, scales, m.p. 104° (Liebermann and Hagen, Ber. 1882, 15, 1428).

Reactions.—It couples in alkaline solution with only 1 mol. of diazotised bases giving 1-*monoazo-* (Kaufler and Brauer, Ber. 1907, 40, 3274) or 1 : 8-*disazo-* dyes (Cassella, D. R.-P. 108166; Eng. P. 9502 of 1899). With nitrous acid it yields the 1-*nitroso-* derivative which with iron salts gives a *naphthol green* (Leonhardt, D. R.-P. 58611). Sulphuric acid at 100° converts it into 2 : 7 - *dihydroxynaphthalene* - 3 : 6 - *disulphonic acid.* It gives 2 : 7-*diaminonaphthalene* by digestion with ammonia at 150°–300°, or by the bisulphite reaction; *phenyl-7-amino-β-naphthol* with aniline at 190°; and the corresponding *diaryl-2 : 7-diaminonaphthalenes* with arylamines (aniline, &c.), and either their hydrochlorides at 140°–150°, or calcium chloride at 280°–300° (Clausius, *l.c.*).

DIHYDROXYNAPHTHALENESULPHONIC ACIDS.

Introductory. — Dihydroxynaphthalenesulphonic acids are seldom obtained by direct sulphonation, and for their preparation recourse is had usually to α- or β-naphthol-di- or trisulphonic acids, to α-naphthylamine-di- or trisulphonic acids *or* to aminonaphtholsulphonic acids.

The exchange of the SO_3H group, or of the NH_2 and SO_3H radicles, for OH in naphthol- or naphthylamine-sulphonic acids is effected by fusion with 60–75 p.c. caustic alkali solution at high temperatures (180°–230°), with results which can be summarised thus:

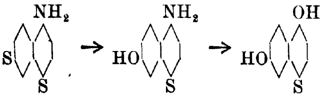
(1) Exchange of the NH_2 for the OH radicle—

In *α-naphthylaminesulphonic acids*, displacement of the NH_2 radicle by OH is achieved most readily when a sulphonic group is present in the 3-, 4- or 5- position. But in *β-naphthylaminesulphonic acids*, the NH_2 radicle is not displaced by OH during fusion with caustic alkali, 2-aminonaphtholsulphonic acids being the final products under ordinary conditions.

(2) Exchange of the SO_3H for the OH radicle—

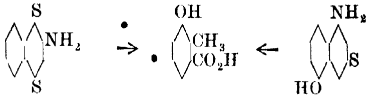
(i.) From *α-naphtholsulphonic acids*, the sulphonic group in the 8- position is the most easily displaced, then that in 5, but that in 2 or 4 resists displacement. From *β-naphtholsulphonic acids*, the sulphonic group in the 4-, 5 or 8-position is easily displaced, but that in 1 or 6 resists displacement.

(ii.) In *α-naphthylaminesulphonic acids*, the order of replaceability follows closely that observed with α-naphtholsulphonic acids. The resistance of a 4-sulphonic group to displacement by OH is displayed, for example, in the products obtained successively from α-naphthylamine-4 : 6-disulphonic acid by fusion with caustic alkali:—

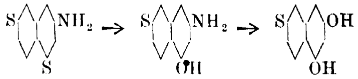


In *β-naphthylaminesulphonic acids* the 4- or 5-sulphonic group is more easily displaced than that in the 8- position, otherwise the order of replaceability agrees with that experienced with the β-naphtholsulphonic acids.

To these rules an important exception exists. Reactions which might be expected to produce 1 : 3-dihydroxynaphthalenesulphonic acids in the alkali fusion, lead almost invariably to decomposition with the formation of hydroxytoluic acids (*cf.* Kalle, D. R.-P. 91201; Eng. P. 16559 of 1894; Höchst, D. R.-P. 81281; 81333).



Turning to *aminonaphtholsulphonic acids* as sources of dihydroxynaphthalenesulphonic acids, those containing an α-amino- group exchange it for OH when heated with water or dilute (5 p.c.) mineral acid under pressure. With β-aminonaphtholsulphonic acids (except 2-amino-3-naphthol-6-sulphonic acid), the exchange takes place only when one of the other constituents, usually the OH radicle, is present in the 4-position:



Apart from these methods, dihydroxynaphthalenesulphonic acids have been obtained, but only in a few instances, from aminonaphtholsulphonic acids by the bisulphite method, and from [α-] or [β-]naphthaquinonesulphonic acids by reduction.

The dihydroxynaphthalenesulphonic acids and their alkali salts are easily soluble in water, the solutions when alkaline usually exhibiting fluorescence. When heated with dilute mineral acids above 200° many of them furnish the corresponding dihydroxynaphthalenes. They give colour reactions with ferric chloride and bleaching powder solutions, being characterised mainly by these and by the azo- dyes produced by coupling with certain diazotised bases. Summaries of the properties of many of the mono- and di-sulphonic acids may be found in the Patent literature (*cf.* Bayer, D. R.-P. 85241 and 79054 respectively).

Azo- dyes.—For the production of azo- dyes, the most valuable of these products are the 1 : 8 - dihydroxynaphthalene - 4 - monosulphonic, and the 2 : 4-, and 3 : 6-disulphonic acids, owing to the fact that the azo- dyes derived from them form lakes with chromium, aluminium or iron mordants (*cf.* Höchst, D. R.-P. 67563; *v.* p. 507). As illustrating the resemblance between the properties of the 1 : 8- and the *ortho*-position, it may be noted that, in this series,[1] the azo- dyes which furnish lakes are derived almost exclusively from the 1 : 2-, 2 : 3- and 1 : 8-dihydroxynaphthalenesulphonic acids (*cf.* for 1 : 2-, Witt, D. R.-P. 49872; for 2 : 3-, Bayer, D. R.-P. 82774). The azo- dyes obtained from 1 : 3 - dihydroxynaphthalene - 5 : 7 - disulphonic acid are remarkable for their yellow shade (*cf.* Bayer, D. R.-P. 78877; Eng. P. 3032 of 1894).

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[1] If the diazotised base be an *ortho*-hydroxy-compound, *e.g.* *o*-aminophenolsulphonic acid, the azo-dyes obtained by coupling it with 1 : 5-dihydroxynaphthalene-2- or 3-sulphonic acid also furnish lakes with chromium salts (Bayer, D. R.-P. 166768).

Dihydroxynaphthalenemonosulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
O : O : S.		
1 : 2 : 4	(1) Reduction of [β-]naphthaquinone-4-sulphonic acid with sulphurous acid (Witt and Kaufmann, Ber. 1891, 24, 3163) (2) Action of sodium bisulphite solution on [β-]naphthaquinone (Bayer, D. R.-P. 70867; Eng. P. 825 of 1893)	*Sodium* salt, needles; *potassium* salt, sp. sol. prisms. Alkaline solution exposed to air turns red, forming 2-*hydroxy*-[α-]*naphthaquinone*. Nitrous acid regenerates [β-]naphthaquinone-4-sulphonic acid. Does not couple (*cf.* Bayer, D. R.-P. 85241).
1 : 2 : 6	Reduction of [β-]naphthaquinone-6-sulphonic acid with sulphurous acid (Witt, Ber. 1891, 24, 3154; D. R.-P. 50506; Paul, Z. angew. Chem. 1897, 10, 51).	*Ammonium* salt NH_4A, readily soluble leaflets. Couples with diazotised bases forming *azo-* dyes, which give lakes with chromium and other oxides (Witt, *l.c.*; D. R.-P. 49872).
1 : 2 : 5 **1 : 2 . 7** **1 : 2 : 8**	These acids obtained by reduction of the corresponding [β-]naphthaquinonesulphonic acids (Witt, Ber. 1891, 24, 3157).	No description published.
1 : 3 : 5	2 - Amino - 4 - naphthol - 8 - sulphonic acid heated with water at 180°–200° (Bayer, D. R.-P. 85241, Eng. P. 3580 of 1895).	*Alkali* salts form yellow solutions which show green fluorescence. Gives dirty green coln. with ferric chloride. Couples with diazotised bases.
1 : 3 : 6	(1) 1-Amino-3-naphthol-6-sulphonic acid heated with water at 120° (Friedländer and Rudt, Ber. 1896, 29, 1613) (2) 2-Amino-4-naphthol-7-sulphonic acid heated with water at 200° (Bayer, D. P. Anm. F. 7978; Eng. P. 25214 of 1894).	*Alkali* salts very soluble; show green fluorescence in alkaline solution; *barium* salt BaA_2, readily soluble needles (Friedländer and Rüdt, *l.c.*). Couples with diazotised bases (*cf.* Bayer, D. R.-P. 81991; Eng. P. 3580 of 1895)
1 : 3 : 7	1 : 3-Dihydroxynaphthalene-5 . 7-disulphonic acid heated with 5 p.c. sulphuric acid under pressure at 210° (Bayer, D. R.-P. 90878).	*Alkali* salts give yellow solutions which show intense green fluorescence. Gives bluish-black coln. with ferric chloride. Couples with diazotised bases (*cf.* Bayer, D. R.-P. 86100; Eng. P. 4962 of 1895).
1 : 5 : 2 **C-acid.**	(1) Together with the 4-acid, when 1 : 5-dihydroxynaphthalene is warmed with sulphuric acid at 50°–60° (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 235). (2) α-Naphthol-2 . 5-disulphonic acid heated with 60 p.c. caustic soda at 250° (Bayer, D. R.-P. 68344; Eng. P. 3397 of 1890).	*Acid sodium* salt, readily soluble leaflets; the alkaline solutions show blue fluorescence. Gives bluish-green colouration with ferric chloride. Couples with diazotised bases (*cf.* Bayer, *l.c.*).
1 : 5 : 3	Naphthalene-1 : 3 : 5-trisulphonic acid fused with caustic alkali (Bayer, D. R.-P. 166768; Eng. P. 18569 of 1902).	Couples with diazotised bases (Bayer, *l.c.*).
1 : 5 : 4	Together with the 2-acid (*q.v.*), when 1 : 5-dihydroxynaphthalene is warmed with sulphuric acid at 50°–60°.	*Calcium* salt forms a sparingly soluble double salt with calcium sulphate. Couples with diazotised bases.
1 : 5 : 7	From 1-amino-5-naphthol-7-sulphonic acid by the bisulphite reaction (Bucherer and Uhlmann, J. pr. Chem. 1909, [ii.] 80, 238; *v.* p. 416)	*Acid*, scales, crystallises with ½ mol. of alcohol. Couples with diazotised bases.
1 : 6 : 3	(1) Fusion of naphthalene-1 : 3 . 6-trisulphonic acid with 90 p.c. caustic soda at 250° (Aktienges., D. R.-P. 42261; Bayer, D. R.-P. 63015; *cf.* Kalle, D. R.-P. 89061). (2) 1-Amino-6-naphthol-3-sulphonic acid heated with water at 200° (Cassella, D. P. Anm. C. 5020). (3) From 2-amino-5-naphthol-7-sulphonic acid by the bisulphite reaction (Badische, D. R.-P. 126136; Eng. P. 1387 of 1900; Bucherer, J. pr. Chem. 1904, [ii.] 69, 83; *v.* p. 416).	*Sodium* salt, sparingly soluble, shows in alkaline solution reddish-blue fluorescence. Gives green colouration with ferric chloride. Forms a yellow easily soluble *nitroso-* compound (Cassella, *l.c.*). Couples with diazotised bases (Bayer, D. R.-P. 85241; Eng. P. 3580 of 1895; Cassella, *l.c.*).
1 : 6 : 4	Fusion of α-naphthylamine-4 : 6-disulphonic acid (Dahl, D. R.-P. 57114; Eng. P. 735 of 1890); *or* of α-chloronaphthalene-4 : 6-disulphonic acid with caustic soda at 210°–220° (Rudolph, D. R.-P. 104902).	*Acid* and *acid sodium* salt, sparingly soluble leaflets; alkaline solutions show violet fluorescence. Forms a sparingly soluble yellow *nitroso-* derivative (Rudolph, *l.c.*) Gives green colouration with ferric chloride. Couples with diazotised bases (Dahl, *l.c.*).
1 : 7 : 3 **G-acid.**	Fusion of β-naphthol-6 : 8-disulphonic acid with caustic soda at 220°–230° (Hochst, D. P. Anm. F. 4153; Eng. P. 9642 of 1889; *cf.* Bayer, D. R.-P. 85241).	*Acid sodium* salt readily soluble needles; alkaline solutions show blue fluorescence. Gives green colouration with ferric chloride. Couples with diazotised bases.

Constitution.	Preparation.	Acids, Salts and Reactions.
O : O : S **1 : 7 : 4**	(1) Fusion of 2-carboxy-α-naphthol-4 : 7-disulphonic acid with caustic alkali at 230°–290° (Bindsch., D. R.-P. 81938; Eng. P. 4629 of 1894). (2) 1.7-Dihydroxy-2-carboxynaphthalene-4-sulphonic acid heated with 30 p.c. caustic soda under pressure at 140°-160° (Bindsch., D. R.-P. 83965).	*Acid* and *acid salts* readily soluble; alkaline solutions show violet fluorescence. Gives green colouration with ferric chloride. Couples with diazotised bases.
1 : 8 : 2	1 - Amino - 8 - naphthol - 7 - sulphonic acid heated with lime and water under pressure at 250° (Bayer, D. P. Anm. F. 7509).	*Acid sodium* salt needles, shows reddish-violet fluorescence in solution. Gives green colouration with ferric chloride. Couples with diazotised bases.
1 : 8 : 3 **ε-acid.**	(1) α-Naphthylamine-3 : 8-disulphonic acid heated with 9 p.c. caustic soda under pressure at 220°–250° (Hochst, D. P. Anm. F. 7112). (2) Digestion of α-naphthol-3 : 8-disulphonic acid or of α-naphthol-6 : 8-disulphonic acid with 50 p.c. caustic soda at 170°–210° (Kalle, D. R.-P. 82422). (3) 1-Amino-8-naphthol-3 5-disulphonic acid heated with water at 200° (Leonhardt, D. P Anm. F. 8626; Eng. P. 19253 of 1895; Cassella, D. R.-P. 108848).	*Acid sodium* salt sparingly soluble needles; alkaline solutions show blue fluorescence (Kalle, *l.c.*). Gives green colouration with ferric chloride (Kalle, *l.c.*). Couples with diazotised bases (*cf.* Bayer, D. R.-P. 85241).
1 : 8 : 4 **S-acid.**	(1) Fusion of the following with caustic alkali or caustic alkali solution: α-naphthol-4 : 8-disulphonic acid (Bayer, D. R.-P. 54116, 67829; Eng. P. 13665, 18517 of 1889) *or* α-naphthol-5 . 8-disulphonic acid, or its sultone (Bayer, D. R.-P 80667; Eng P. 1227 of 1894); also of α-naphthylamine - 4 : 8 - disulphonic acid (Bayer, D. R.-P. 71836; Badische, D. R.-P 91855; Eng. P. 9894 of 1893), *or* α-naphthylamine - 5 : 8 - disulphonic acid (Bayer, D. R.-P. 77285, Eng P 1227 of 1894), also of 1-amino-8-naphthol-4-sulphonic acid (Bayer, D. R.-P. 75319; 80315); *or* 1-amino-8-naphthol-5-sulphonic acid (Bayer, D. R.-P. 75055; Eng. P. 15269 of 1893). (2) 1 : 8 - Diaminonaphthalene-4-sulphonic acid heated with milk of lime at 230° (Cassella, D R.-P. 75962) (3) From 1-amino-8-naphthol-4-sulphonic acid (Bayer, D. R.-P. 109102; Eng. P. 16807 of 1899), or 5-sulphonic acid (Bucherer, J. pr. Chem 1904, [ii.] 69, 86) by the bisulphite reaction (*v* p 416).	*Acid* forms three series of salts, all easily soluble; *monosodium* salt NaH_2A, silky leaflets; *disodium* salt Na_2HA+2H_2O, leaflets; *monobarium* salt BaH_4A_2, needles; *dibarium* salt $BaHA+1\frac{1}{2}H_2O$ (Bayer, D R.-P. 67829; Eng. P. 13665 of 1889) Basic salts (*trisodium*, &c.) show bluish-green fluorescence in solution. Gives dirty green precipitate with ferric chloride. Couples with diazotised bases, giving *azo-* dyes which have the property of forming lakes with chromium and other oxides (*cf.* Bayer, D. R.-P. 61707; 67829; 66693; Eng P. 5984 of 1891). For *monoalkyl* derivatives and for *azo-* dyes obtained by coupling them with diazotised bases, *cf.* Bayer, D. R.-P. 73741; 78937; Eng. P. 3495 of 1893.
2 : 3 : 6 **R-acid.**	Fusion of β-naphthol-3 : 6-disulphonic acid with caustic soda at 240°–280° (Badische, D. R.-P. 57525; Eng. P. 15803 of 1890; Hochst, D. P. Anm. F. 4153; Eng. P. 9642 of 1889; Friedlander and Zakrzewski, Ber. 1894, 27, 762).	*Acid sodium* salt, sp sol leaflets, shows reddish-blue fluorescence in alkaline solution; *barium* salt, BaA_2, sp. sol. (*cf.* Bayer, D. R.-P. 85241). Gives intense violet coln. with ferric chloride. Couples with diazotised bases, giving *azo-* dyes which form lakes with metallic oxides (*cf.* Bayer, D. R.-P. 82774).
2 : 7 : 3[1] **F-acid.**	Fusion of β-naphthol-3 : 7-disulphonic acid with caustic alkali (*cf.* Aktienges., D. R.-P. 63956; Bayer, D. R.-P. 85241).	*Sodium* salt, sparingly soluble crystalline powder, shows bluish-violet fluorescence in solution. Gives deep blue colouration with ferric chloride.

Dihydroxynaphthalenedisulphonic Acids.

Constitution.	Preparation.	Acids, Salts and Reactions.
O : O : S : S **1 : 2 : 3 : 6**[2] and **1 : 2 : 6 : 8**	(1) Acid sodium salt of 1-amino-2-naphthol-3 : 6- (resp. 6 : 8-)disulphonic acid boiled with water (Witt, Ber. 1888, 21, 3480; D. R.-P. 49857). (2) Reduction of [β-]naphthaquinone-3 : 6- (resp. 6 : 8-)disulphonic acid with sulphurous acid (Witt, Ber. 1891, 24, 3157).	*Acid sodium* salts, readily soluble leaflets; decompose very rapidly in alkaline solution (*cf.* Bayer, D. R.-P. 79054). Do not couple with diazotised bases (Bayer, *l.c.*; *cf* Witt, Ber. 1891, 24, 3156). Precipitate gelatin or basic aniline dyes from solution (*naphthatannins*; *cf.* Witt, D. R.-P. 49857).

[1] The acid described as 2 : 6-dihydroxynaphthalene-4-sulphonic acid (Bayer, D. R.-P. 72222) is considered by Jacchia to be a disulphonic acid (Annalen, 1902, 323, 131).

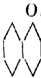
[2] The 1 : 2-dihydroxynaphthalene-3 : 6-disulphonic acid is also formed when 1 : 2-diaminonaphthalene-3 : 6-disulphonic acid is heated with dilute mineral acids (*cf.* Cassella, D. R.-P. 72584).

Constitution.	Preparation.	Acids Salts and Reactions.
O : O : S : S		
1 : 3 : 5 . 7 **Yellow acid.**	(1) Mixed with 30 p.c. of 'red' acid, by heating naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid *or* α-naphthol-3 : 5 : 7-trisulphonic acid with 60 p.c. caustic soda at 180°–200° (Bayer, D. R.-P. 79054; 80464, Eng P. 25074 of 1893). (2) 2-Amino-4-naphthol-6 : 8-disulphonic acid heated with water under pressure at 210°–220° (Bayer, D. R.-P. 89242).	*Sodium* salt, readily soluble; *potassium* salt, leaflets; alkaline solutions show green fluorescence; *barium* salt BaA, moderately soluble needles (Friedlander and Rudt, Ber. 1896, 29, 1613). Gives blue colouration with ferric chloride. Couples in alkaline solution with diazotised bases, giving *azo-* dyes of yellow shade.(*cf.* Bayer, D. R -P. 78877; Eng. P. 3032 of 1894).
1 : 5 : 3 : 7 **Red acid.**	(1) α - Naphthol - 3 . 5 : 7 - trisulphonic acid heated with 50 p c. caustic soda at 150°–160° (Kalle, D. P. Anm. K 12732) (2) Mixed with 70 p c. of 'yellow' acid from naphthalene-1 : 3 . 5 . 7-tetrasulphonic acid and 60 p.c. caustic soda at 180°–200°.	*Potassium* and *sodium* salts readily soluble needles in alkaline solution shows bluish-violet fluorescence (Bayer, D. R.-P. 79054). Gives bluish-green coln with ferric chloride. Couples in acid or alkaline solution (*cf* Bayer, *l.c.*) with 1 or 2 mols. (*cf.* Kalle, *l.c.*) of diazotised bases, giving *azo-* dyes
1 : 5 : (2) : (4)	1 : 5 - Dihydroxynaphthalene sulphonated with sulphuric acid at 100°–160° or with anhydro-acid in the cold (Ewer and Pick, D. R.-P. 41934).	No description published, but acid said to couple with diazotised bases (Ewer and Pick, *l.c.*; *cf.* 2- and 4-monosulphonic acids).
1 :(7):(2):(4)	Fusion of α-naphthol-2 : 4 · 7-trisulphonic acid with caustic alkali (*cf.* Hochst, D. R.-P. 67426; Eng. P. 18783 of 1891)	No description published. Couples with diazotised bases (Hochst, *l.c.*).
1 : 7 : 3 : 6 **A-acid.**	Mixed with 30 p.c. of the 2 . 3 : 6 . 8-acid, by fusion of β-naphthol-3 : 6 : 8-trisulphonic acid with caustic alkali at 230°–240° (Hochst, D P Anm F. 4154; Eng P. 9642 of 1889; D R -P 67563; *cf* Friedlander and Silberstern, Monatsh. 1902, 23, 527).	*Sodium* salt Na_2A, sparingly soluble needles; alkaline solutions show bluish-green fluorescence. Forms a dark blue precipitate with formaldehyde and hydrochloric acid (Friedländer and Silberstein, *l c.*) Gives fleeting blue coln with ferric chloride (*ibid.*). Couples with diazotised bases (Hochst, *l.c.*).
1 : 8 : 2 : 4 **S-acid.**	(1) 1-Amino-8-naphthol- or naphthasultam-2 : 4-disulphonic acid heated with 80 p c. caustic soda solution at 250° (Bayer, D. R -P. 77703, Eng. P 4970 of 1893, Cassella, D R. - P. 81282; Dressel and Kothe, Ber. 1894, 27, 2142) (2) 1-Amino-8-naphthol-5 . 7-disulphonic acid heated with dilute caustic soda solution above 250° (Badische, D. P. Anm. B. 16142; Eng. P 18924 of 1893) (3) Fusion of α-naphthol-2 4 . 8-trisulphonic acid with caustic alkali at 210° (Bayer, D. R.-P. 57021; Eng P 3367 of 1890; Dressel and Kothe, Ber. 1894, 27, 2144).	*Disodium* salt readily soluble needles, showing faint blue fluorescence in solution; *trisodium* salt Na_3HA+4H_2O, readily soluble prisms, formed in alkaline solution, shows greenish fluorescence (Dressel and Kothe, *l.c.*). Forms a soluble orange *mononitroso-* compound (Cassella, *l c*; Dressel and Kothe, *l.c.*). Gives green colouration with ferric chloride (*cf.* Badische, *l c*) Couples with diazotised bases (*cf.* Bayer, D. R.-P. 73551; Eng P. 18517 of 1889). In acid solution with dichromate gives black dye on wool (Cassella, *l.c.*).
1 : 8 : 3 : 5 **K-acid.**	(1) Fusion of α-naphthol-4 : 6 : 8-trisulphonic acid with 70 p.c caustic soda solution under pressure at 170°–190° (Bayer, D. P. Anm. F. 7004; Eng. P 17141c of 1893; *cf* Kalle, Eng P 1641 of 1894). (2) 1-Amino-8-naphthol-3 · 5-disulphonic acid heated with 7 p.c. caustic soda solution under pressure at 210° (Leonhardt, D. P. Anm. F. 8682; Eng P 21919 of 1895; Cassella, D. R.-P. 108848). (3) 1-Amino-8-naphthol-4 : 6-disulphonic acid heated with 70 p.c. caustic alkali solution above 240° (Bayer, D. R.-P. 80741; Eng. P. 171410 of 1893).	*Disodium* salt readily soluble needles; solutions of *acid salts* show faint blue fluorescence (*cf.* Bayer, D. R.-P. 79054). Forms a readily soluble yellow *nitroso-* derivative. Gives green colouration with ferric chloride (Bayer, *l c*). Couples with diazotised bases (Bayer, D. P. Anm. F. 7004; Eng. P 17141c of 1893).
1 : 8 : 3 : 6 **Chromotrope acid**	(1) α-Naphthol-3 : 6 : 8-trisulphonic acid or its sultone heated with 60 p.c. caustic soda at 170°–220° (Hochst. D. R.-P. 67563). (2) 1-Amino-8-naphthol-3 : 6-disulphonic acid heated with 5 p.c. caustic soda under pressure at 265° (Bayer, D. R -P. 68721; Eng. P. 11522 of 1892). (3) 1 : 8-Diaminonaphthalene-3 : 6 - disulphonic acid heated with 5 p.c. caustic soda under pressure at 260°–280° (Bayer, D. R.-P. 69190; Eng. P. 11522 of 1892), or with dilute mineral acids or water under pressure at 150°–160° (Cassella, D. R.-P. 75153). (4) 8-Chloro-α-naphthol-3 : 6-disulphonic acid fused with caustic alkali (Badische, D. R.-P. 147852).	*Acid* forms four series of salts, two strongly acid, one neutral, one basic. *Disodium* salt $Na_2H_2A+2H_2O$, readily soluble in water, and acid towards sodium carbonate; alkaline solutions show violet-blue fluorescence. *Barium* salt BaH_2A+3H_2O, small leaflets, which in solution with sodium carbonate yields the *sodium barium* salt $BaNaHA+3H_2O$, in needles (Hochst, *l.c.*). Gives grass-green coln. with ferric chloride (*ibid.*). Couples with 1 or 2 mols. of diazotised bases, giving ortho-*azo-* dyes (Hantower and Täuber, Ber. 1898, 31, 2156) which form lakes with chromium salts (*cf.* Höchst, D. R.-P. 59161). In acid solution with dichromate gives brown dye on wool (Hochst, D. R.-P. 77552). For *monoalkyl* derivatives, *cf.* Bayer, D. R.-P. 73251; 73741; Eng. P. 3493 of 1893. For, *chloro-* derivative and derived *azo-* dyes, *cf.* Höchst, D. R.-P. 153195.

Constitution.	Preparation.	Acids, Salts and Reactions.
O : O : S : S **1 : 8 : ? : ?** **I-acid.** **1 : 8 : ? : ?** **G-acid.** **1 : 8 : ? : ?** **R-acid.**	1 : 8 - Dihydroxynaphthalene sulphonated with sulphuric acid at 50° and the respective products separated by means of their barium salts, of which that of I-acid is least and of R-acid most soluble (Badische, Eng. P. 14294 of 1891 ; D. R.-P. 79029 ; 79030).	*Sodium* salts very readily soluble, show blue fluorescence in alkaline solution. Give green colourations with ferric chloride. Couple with diazotised bases, forming *azo-* dyes, which, if from I-acid are worthless, but from G-acid valuable (*cf.* Bayer, D. R.-P. 79054).
2 : 3 : 6 : 8 **B-acid.**	Mixed with the 1 : 7 : 3 : 6-acid, by fusion of β-naphthol-3 : 6 . 8-trisulphonic acid with caustic alkali and separated from the less soluble isomeride by fractional precipitation with brine (Hochst, D R.-P. 67563 ; *cf.* Friedländer and Silberstern, Monatsh., 1902, 23, 527).	*Sodium* salt $Na_2A + 3\frac{1}{2}H_2O$, easily soluble needles, shows bluish-violet fluorescence in alkaline solution ; *barium* salt BaA, sp sol needles. Gives violet coln. with ferric chloride, but no precipitate with formaldehyde and hydrochloric acid (Friedlander and Silberstern, *l.c.*). Couples with diazotised bases (*ibid.*).
2 : 7 : 3 : 6	(1) 2 : 7-Dihydroxynaphthalene sulphonated with sulphuric acid on a water bath (Aktienges , D. R.-P. 75142 ; Eng. P. 16199 of 1893). (2) β - Naphthol - 3 : 6 : 7 - trisulphonic acid heated with 66 p.c. caustic soda solution under pressure at 220°–300° (Bayer, D. P. Anm. F. 7243 ; Eng. P. 25074A of 1893).	*Acid sodium* salt moderately soluble ; *potassium* salt, large needles , *barium* salt, almost insoluble ; salts show bluish-green fluorescence in alkaline solution (*cf.* Bayer, D. R -P. 79054). Forms a sp. soluble orange *nitroso-* compound. Gives deep blue colouration with ferric chloride. Couples in alkaline solution with 1 mol. of diazotised bases (Bayer, D. P. Anm. F. 7243).

TRIHYDROXYNAPHTHALENES.

Introductory.—The trihydroxynaphthalenes have little technical interest. The methods available for their production are fusion of naphthalene- or naphthol-sulphonic acids with caustic alkali, and reduction of hydroxynaphthaquinones, but the number of isomerides they can give is limited by the small number of acids or quinones available. Only six of the fourteen isomeric trihydroxynaphthalenes have been isolated and characterised, but sulphonic acids of two others are known. The azo-dyes obtained from those that couple with diazotised bases are unimportant.



(i.) 1 : 2 : 3-**Trihydroxynaphthalene** (*Naphthapyrogallol*), obtained by boiling *iso*naphthazarin with zinc and dilute sulphuric acid (Zincke and Ossenbeck, Annalen, 1899, 307, 18), is crystalline, and gives a *triacetate*, in prisms, m.p. 250°–255° (Zincke and Noack, Annalen, 1897, 295, 19).

(ii.) 1 : 2 : 4-**Trihydroxynaphthalene**, formed by reduction of hydroxy-[α-]naphthaquinone with tin and hydrochloric acid (Graebe and Ludwig, Annalen, 1870, 154, 324) ; *or* by hydrolysis of the triacetate with alcoholic hydrogen chloride (Thiele and Winter, Annalen, 1900, 311, 346 ; Bayer, D. R.-P. 101607 , Eng. P. 10590 of 1898), crystallises in needles, m.p. 154°, and in alkaline solution absorbs oxygen giving *hydroxy*-[α-]*naphthaquinone.*

The *triacetate*, obtained by heating [α-] or [β-]naphthaquinone and acetic anhydride with a small quantity of sulphuric acid (Bayer, *l.c.* ; Thiele and Winter, *l.c.*) or phosphoric acid (Bayer, D. R.-P. 107508 ; Eng. P. *l.c.*) at 30°–40°, or zinc chloride at 50°–60° (Thiele and Winter, *l.c.*), crystallises in needles, m.p. 134°–135°.

(iii.) 1 : 3 : 5 - Trihydroxynaphthalene, unknown. The 7-**sulphonic acid** is formed when naphthalene-1 : 3 : 5 : 7-tetrasulphonic acid (*or* the α-naphthol-3 : 5 : 7-trisulphonic acid *or* the 1 : 3- or 1 : 5-dihydroxynaphthalenedisulphonic acid obtainable from it) is fused with caustic potash at 280° (Bayer, D. R.-P. 80464 ; Eng. P. 19624 of 1893). Its *potassium* salt separates in needles, and couples with 1 or 2 mols. of a diazotised base, forming *azo-* dyes (Bayer, D. R.-P. 87583 ; Eng. P. 1229 of 1894).

(iv.) 1 : 3 : 6 - **Trihydroxynaphthalene,**[1] obtained by fusing 1 : 6-dihydroxynaphthalene-3-sulphonic acid with caustic soda at 250°–270° (Kalle, D. R.-P. 112176 ; Meyer and Hartmann, Ber. 1905, 38, 3950) forms doubly refracting crystals, m.p. 95° ; a *hydrochloride* in yellow needles ; and a *triacetate*, needles, m.p. 112°–113°. It couples with diazotised bases forming *azo-* dyes.

(v.) 1 : 3 : 8 - Trihydroxynaphthalene, unknown. The 6-**sulphonic acid**, obtained by fusing α-naphthol-3 : 6 : 8-trisulphonic acid, or 1 : 8 - dihydroxynaphthalene - 3 : 6 - disulphonic acid with caustic potash at 310°–320°, forms easily soluble alkali salts, which show greenish-blue fluorescence in solution, and couple with 1 or 2 mols. of a diazotised base forming *azo-*dyes (Bayer, D. R.-P. 78604 ; Eng. P. 17141c of 1893),

(vi.) 1 : 4 : 5-**Trihydroxynaphthalene** ([α-[*hydrojuglone*), mixed with about one-fifth the amount of [β-]hydrojuglone, is present in the shell of the walnut, whether ripe or unripe, and is insoluble, whereas the [β-] form is easily soluble in chloroform (Mylius, Ber. 1884, 17, 2412 ; 1885, 18, 2568). If merely melted the [α-] compound gives an equilibrium mixture containing about 75 p.c. of the [β-] form, while an alkaline solution of the latter regenerates the [α-] compound on acidification, the isomerism being keto-enolic (Willstatter and Wheeler, Ber. 1914, 47, 2796). The [α-] compound separates from water in scales or needles, m.p. 148° (Mylius, m.p. 168°–170°). With ferric chloride it gives *juglone*, and with acetic anhydride yields the *triacetate* of the [β-] form in prisms, m.p. 129°–130°. [β-]*Hydrojuglone* crystallises in hexagonal tablets, m.p. 96°–97°.

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[1] A polymeride $C_{20}H_{10}(OH)_6$, possibly a dinaphthyl derivative, of which the *hexacetate* crystallises in scales m.p. 200°, is formed by boiling the aqueous solution of this trihydroxynaphthalene (Kalle, *l.c.* ; Meyer and Hartmann, *l.c.*).

(vii.) 1 : 4 : 6 - **Trihydroxynaphthalene**, obtained by reducing 6-hydroxy-[α-]naphthaquinone with stannous chloride, forms star-like groups of needles, m.p. 138°–140°, highly oxidisable; the *triacetate*, needles, m.p. 94°–95° (Fischer and Bauer, J. pr. Chem. 1916, [ii.] 94, 8).

(viii.) 1 : 6 : 7 - **Trihydroxynaphthalene**, obtained when 1 : 6 : 7-trihydroxynaphthalene-3-sulphonic acid is heated with water or 5 p.c. sulphuric acid under pressure at 210°-220° (Cassella, D. R.-P. 112098; Eng. P. 27345 of 1898; Friedländer and Silberstern, Monatsh. 1902, 23, 530), forms needles, m p. 175°; its *triacetate*, needles, m.p. 143°-144°; and *trimethyl ether*, prisms, m.p. 127°-128°. It couples in the 4-position with 1 mol. of a diazotised base, giving *azo-* dyes which form lakes with chromium or iron salts (Cassella, D. R.-P. 110618; Eng. P. *l.c.*; D. R.-P. 110904).

The 3-sulphonic acid, prepared from β-naphthol-3 : 6 : 8-trisulphonic acid by prolonged fusion with caustic alkali at 240°–250°, gives a *barium* salt BaA_2 in sparingly soluble leaflets, a *sodium* salt in sparingly soluble needles, and with formaldehyde and hydrochloric acid a violet precipitate (Friedländer and Silberstern, *l.c.*). With diazotised bases it couples, forming *azo-* dyes (*cf.* Höchst, D. R.-P. 67426; Eng. P. 18783 of 1891).

AMINODIHYDROXYNAPHTHALENES.

The aminodihydroxynaphthalenes are of interest chiefly in relation to hydroxynaphthaquinoneoximes (nitrosodihydroxynaphthalenes) and have no technical value. Little is known about them, the hydrochloride and the triacetyl derivative being almost the only definite substances isolated in each case.

N : O : O	$[NH_2{\cdot}C_{10}H_5(OH)_2]$
1 : 2 : 3	Decomp. 230° (Friedlander and Silberstern, Monatsh 1902, 23, 521)
1 : 2 : 4[1] [4 : 1 : 3]	Not isolated. *Triacetyl* derivative, tablets, m.p. 155°–156° (Kehrmann and Hertz, Ber 1896, 29, 1419).
1 : 2 : 6	Not isolated Obtained by reduction of azo- derivative of 2 · 6-dihydroxynaphthalene (Kehrmann, Ber 1907, 40, 1962) The 4-sulphonic acid is obtained by reduction of 1-nitroso-2 . 6-dihydroxynaphthalene with sodium bisulphite solution (Bayer, D. R.-P. 87900; Eng. P. 6035 of 1893).
1 : 2 : 7	Not isolated. Obtained by reduction of nitroso-2 : 7-dihydroxynaphthalene (Clausius, Ber. 1890, 23, 521). *Triacetyl* derivative, m p 183°; *tetra-acetyl* derivative, m.p. 135° (Nietzki and Knapp, Ber. 1897, 30, 1123). 7-*Methyl* ether, leaflets, m.p 170°; 2 : 7-*dimethyl* ether, needles, m p. 82°-83° (Fischer and Kern, J. pr. Chem. 1916, [ii] 94, 26). The 4-sulphonic acid is obtained by reduction of 1-nitroso-2 . 7-dihydroxynaphthalene with sodium bisulphite solution (Bayer, *l.c.*).
1 : 3 : 4 [4 : 1 : 2]	Not isolated. *Triacetyl* derivative, prisms, m.p. 193° (Kehrmann, Ber. 1894, 27, 3340).
1 : 4 : 7 [4 : 1 : 6]	Easily oxidisable (Fischer and Bauer, J. pr. Chem. 1916, [ii] 94, 7).
1 : 5 : 8 [5 : 1 : 4]	Not isolated. *Triacetyl* derivative, needles, m.p. 165° (Graebe and Oeser, Annalen, 1904, 335, 149).
1 : (6) : 8 [8 : 1 : (3)]	Unknown. The (3)-sulphonic acid, obtained by fusing 1-amino-8-naphthol-3 : 6-disulphonic acid with 60 p.c. caustic soda solution at 210°, is diazotisable (Bayer, D. R.-P. 75097).
2 : 1 : 4	Not isolated. *Triacetyl* derivative, needles, m.p. 259°–260° (Kehrmann, Ber. 1894, 27, 3343).
2 : 1 : 5	Stellate groups (Fischer and Bauer, J. pr. Chem. 1917, [ii.] 95, 262). Very sensitive to light.
2 : 1 : 6	Unstable. *Triacetyl* derivative, needles, m p. 150° (Fischer and Bauer, J. pr. Chem. 1916, [ii.] 94, 5).
2 : 3 : 4 [3 : 1 : 2]	Needles, m.p 164°. *Triacetyl* derivative, needles, decomp. above 200° (Zincke and Noack, Annalen, 1897, 295, 13).
2 : (3) : 8 [7 : 1 . (6)]	Unknown. The (6)-sulphonic acid, obtained by fusing 2-amino-8-naphthol-3 : 6-disulphonic acid with caustic alkali at 240°-280°, is diazotisable (Höchst, D. R.-P. 53023; Eng. P. 15175 of 1889).

TETRAHYDROXYNAPHTHALENES.

1 : 2 : 3 : 4-**Tetrahydroxynaphthalene** (*Leucoisonaphthazarin*), obtained from *iso*naphthazarin by reduction, forms easily soluble scales, and its *tetra-acetyl* derivative, needles, m.p. 220°. It is readily oxidised to *iso*naphthazarin, and reduced to 1 : 2 : 3-*trihydroxynaphthalene* (Zincke and Ossenbeck, Annalen, 1899, 307, 16).

1 : 2 : 5 : 8-**Tetrahydroxynaphthalene** (*Leuconaphthazarin*) obtained when naphthazarin is boiled with alcohol, stannous chloride, and hydrochloric acid (Zincke and Schmidt, Annalen, 1895, 286, 37); or when a boiling aqueous solution of 'naphthazarin melt' is reduced by iron (Badische, D. R.-P. 129074; Eng. P. 23887 of 1900), forms needles, m.p. 154°, and its *tetra-acetyl* derivative, minute prisms, m.p. 277°–279° (Schunck and Marchlewski, Ber. 1894, 27, 3463; Zincke and Schmidt, *l.c.*; Liebermann, Ber. 1895, 28, 1457; *cf.* Wheeler and Edwards, J. Amer. Chem. Soc. 1916, 38, 387). It is readily oxidised to naphthazarin, and is a substantive dye which when oxidised with chromic acid on the fibre gives black shades (Badische, *l.c.*).

DIAMINODIHYDROXYNAPHTHALENES.

Several diaminodihydroxynaphthalenes have been described, but only those which furnish clues to the constitution of disazo- dyes obtained from dihydroxynaphthalenes need be mentioned here.

1 : 4-Diamino-2 · 3-dihydroxynaphthalene, obtained by reduction of disazo-dye from 2 : 3-dihydroxynaphthalene, forms *sulphate*, $B{\cdot}H_2SO_4$, leaflets, and gives *isonaphthazarin* with ferric chloride (Friedländer and Silberstern, Monatsh, 1902, 23, 524).

1 : 6-Diamino-4 : 5-dihydroxynaphthalene, obtained by reduction of disazo- dye from 1 : 8-dihydroxynaphthalene, is very rapidly oxidised to naphthazarin (*ibid* 518).

1 : 8-Diamino-2 : 7-dihydroxynaphthalene, obtained by reduction of disazo- dye from 2 : 7-dihydroxynaphthalene, gives *sulphate*, needles, which forms blue solution in alkalis (Cassella, D. R.-P. 108166; Eng. P. 9502 of 1899).

IX. QUINONE DERIVATIVES.

Introductory.—From the formula of naphthalene the existence of three homo- and three hetero- nucleal quinones may be predicted. Two of the homonucleal naphthaquinones together with derivatives of the third (2 : 3-) are known, but only one of the heteronucleal compounds

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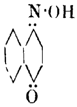
[1] An amino-1 : 3-dihydroxynaphthalene, m.p. 162°, which may have this constitution, has been described by Zincke and Wiegand (Annalen, 1895, 286, 89); and a second, possibly the 2-amino-1 : 3-derivative, has been isolated by Friedländer and Rüdt (Ber. 1896, 29, 1611).

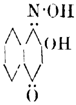
(2 : 6-) has been isolated.[1] A comparison shows that in physical properties 1 : 4- or [α-] naphthaquinone, but in chemical properties 2 : 6-naphthaquinone, most closely resembles ordinary *para*-benzoquinone, whereas 1 : 2- or [β-] naphthaquinone exhibits the general characters of an *ortho*-diketone.

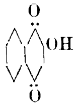
The naphthaquinones are coloured substances, and, with few exceptions, give rise to derivatives, which also are coloured, but only a small proportion of them are dyes. The auxochromes, which endow naphthaquinone derivatives with the property of forming coloured lakes, are associated with contiguous carbon atoms, *i.e.* are present relatively in the *ortho*-position.[2] For quinones, these auxochromes have been shown by Kostanecki (Ber. 1887, 20, 3147; 1889, 22, 1349) to be the following:—

$$\begin{array}{llll} \cdot C:O & \cdot C:N\cdot OH & \cdot C:N\cdot OH & \cdot C:N\cdot OH \\ :\dot{C}\cdot OH & :\dot{C}\cdot OH & \cdot\dot{C}:O & \cdot\dot{C}:N\cdot OH \end{array}$$

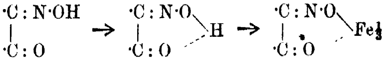
To illustrate their effect, reference may be made to the following series of [α-]naphthaquinone derivatives in which I is not a dye, but II and III form coloured lakes with basic mordants:—

I


II


III


In the more recent discussion of the subject (*cf.* Tschugaeff, J. pr. Chem. 1907, [ii.] 76, 88; Werner, Ber. 1908, 41, 1062, 2383; Liebermann, *ibid.* 1436; Morgan, J. Soc. Dyers and Col. 1921, 37, 43), the production of lakes by compounds of these types is referred to the formation of complex heterocyclic groups, in which the metal of the mordant forms one component of the 5- or 6- membered ring. But cyclic structure is not of itself sufficient to develop colour with basic mordants, and in each auxochrome complex there is also present a radicle, which by its 'subsidiary' valency can be linked with the metal. For example, [β-]naphthaquinoneoxime (1-nitroso-β-naphthol) is a dye, because in it the oxygen atom of the carbonyl group has residual valency, and through this residual or 'subsidiary' valency (shown in the formula by the dotted line) becomes linked to the metal of the mordant:—



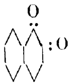
Oxime

Lake (naphthol green)

Lakes are remarkable not only on account of their colours but of their insolubility and fastness and of the non-ionisable state of the metallic radicle contained in them.

Naphthaquinoneoximes, obtainable from the quinones by interaction with hydroxylamine, are usually made from the naphthols or from dihydroxynaphthalene derivatives by means of nitrous acid. As the chief interest attaching to these substances from the technical side lies in the colouring matters to which some of them give rise, they are described in this article as nitrosonaphthols, following the Patent literature, although classified as oximes.

NAPHTHAQUINONES.



(i.) 1 : 2-**Naphthaquinone** ([β-] *naphthaquinone*) is obtained by the oxidation *either* of 1-amino-2-naphthol with chromic acid mixture (Stenhouse and Groves, Chem. Soc. J. 1878, 33, 415; Liebermann and Jacobson, Annalen, 1882, 211, 49; Grandmougin and Michel, Ber. 1892, 25, 982; Paul, Z. angew. Chem. 1897, 10, 24; Russig, J. pr. Chem. 1900, [ii.] 62, 56), or with ferric chloride (Groves, Chem. Soc. Trans. 1884, 45, 298; Paul, *l. c.* 48) *or* of 2-amino-1-naphthol by nitrous acid (Grandmougin and Michel, *l.c.* 3430).

Preparation.—Freshly-prepared 1-amino-2-naphthol, obtained by reduction of Orange II (100 grms.) with sodium hypo(hydro)sulphite, is dissolved or suspended in sulphuric acid of sp. gr. 1·2 (200 c.c.) and oxidised in the cold by a solution of sodium dichromate (30 grms.) in water (Grandmougin, Ber. 1906, 39, 3561). Or the freshly prepared product, obtained from β-naphthol (50 grms.) by reducing its nitroso-compound with hydrogen sulphide, is dissolved in 5 p.c. sulphuric acid (1400 c.c.) and oxidised in the cold with a solution of potassium dichromate (35 grms.) in water (Lagodzinski and Hardine, Ber. 1894, 27, 3076). The yield amounts to about 25 p.c. of the weight of the Orange II (*p*-sulphobenzeneazo-β-naphthol), or to about 80 p.c. of that of the β-naphthol employed.

Identification.—It crystallises in red needles or in orange scales, decomposes with blackening at 115°–120° (Liebermann and Jacobson, *l.c.*), and resembles [α-]naphthaquinone in solubility, but differs from it by being destitute of odour and non-volatile with steam. Dilute alkalis dissolve it, forming yellow solutions, which rapidly become dark on being shaken with air.

Reactions.—By sulphurous acid, or dilute hydriodic acid, it is reduced to 1 : 2-*dihydroxynaphthalene*, but stannous chloride converts it into *β-dinaphthyldihydroquinone* (Stenhouse and Groves, *l.c.*). Oxidation with ferric chloride in 10 p.c. aqueous solution gives *di-*[*β-*]*naphthaquinone oxide* (Wichelhaus, Ber. 1897, 30, 2199)

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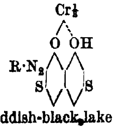
[1] The compound described as 1 : 8- or *per*naphthaquinone by Meldola and Hughes (Chem. Soc. Trans. 1890, 57, 632) is now known to be a *dinaphthaquinone* (Liebermann and Schlossberg, Ber. 1899, 32, 546; *cf.* Meldola, *ibid.* 868).

[2] In the naphthalene series, azo- dyes which, when chromed, give rise to lakes are derived for the most part either

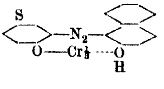
(*a*) from 1 : 2-, 2 : 3- or 1 : 8-dihydroxynaphthalenes and their sulphonic derivatives by coupling with diazotised bases or

(*b*) from diazo-oxides by coupling with β-naphthol or with the 1 . 5-, 1 : 7- and 2 : 6-dihydroxynaphthalenes and their sulphonic acids.

The determining factor in the production of these lakes is the propinquity of the hydroxyl groups, as is evident from the formulæ of the following dyes (one from each source) which before chroming give bluish-red shades on wool:—



reddish-black lake



bluish-black lake

(*Cf.* Morgan, J. Soc. Dyers and Col. 1921, 37, 46; Morgan and Porter, Chem. Soc. Trans. 1915, 107, 651).

and with nitric acid of sp. gr. 1·38 successively 3-*nitro-*[β-]*naphthaquinone* (Zaertling, Ber. 1890, 23, 175) and *phthalic acid* (Stenhouse and Groves, *l.c.*), but with permanganate or dichromate only *phthalic acid* (Boswell, J. Physical Chem. 1907, 11, 119).

With phenylhydrazine it gives the *hydrazone* [O : N_2HPh = 1 : 2], red needles, m.p. 138°, isomeric with benzeneazo-β-naphthol (Zincke and Rathgen, Ber. 1886, 19, 2483; Bamberger, Ber. 1897, 30, 514). With hydroxylamine it forms the *monoxime*, identical with 2-nitroso-α-naphthol (Goldschmidt, Ber. 1884, 17, 215). With aniline in alcoholic solution it yields 2-*hydroxy-*[α-]*naphthaquinoneanil* [O : OH : NPh = 1 : 2 : 4], m.p. above 240°, red needles, soluble in alkali, and convertible into 2-*anilino-*[α-]*naphthaquinone*, m.p. 190°–191°, red needles, insoluble in alkali (Liebermann and Jacobson, *l.c.*; Zincke, Ber. 1881, 14, 1294).

Acetic anhydride aided by sulphuric acid or zinc chloride or phosphoric acid, converts it at 50° into the *triacetate* of 1 : 2 : 4-trihydroxynaphthalene. With sodium bisulphite solution of sp.gr. 1·4 it gives 1 : 2-*dihydroxynaphthalene-*4-*sulphonic acid* at the ordinary temperature and, with sodium thiosulphate and acetic acid, 1 : 2-*dihydroxynaphthalene-*4-*thiosulphonic acid* (Bayer, D. R.-P. 71314; Eng P. 825 of 1893). When heated with sulphuric acid, with or without the presence of boric acid, at 125°–150°, it is converted into *naphthaquinone black*, which dyes mordanted wool in black shades (Heyden, D. R.-P. 113336; Eng P. 3265 of 1900).

(ii.) 1 : 4-**Naphthaquinone** ([α-]*naphthaquinone*) can be obtained by oxidation of naphthalene with chromic acid in acetic acid solution (Groves, Chem. Soc. J. 1873, 26, 209). It is also formed when α-naphthyl acetate (Miller, Ber. 1881, 14, 1601), *or* 1-amino-4-naphthol (Liebermann, Ber. 1881, 14, 1796); *or* α-naphthylamine, *or* dimethyl-α-naphthylamine, *or* α-naphthylamine-4-sulphonic acid (Monnet, Reverdin and Noelting, Ber. 1879, 12, 2306) is oxidised with chromic acid mixture, *or* 1 : 4 diaminonaphthalene with nitrous acid (Grandmougin and Michel, Ber. 1892, 25, 977).

Preparation.—It is prepared conveniently from 1-amino-4-naphthol by oxidation with potassium dichromate and dilute sulphuric acid, the yield amounting to about 40 p.c. of that calculated (Liebermann and Jacobson, Annalen, 1882, 211, 61), but can be obtained in equally good yield from naphthalene by oxidation in concentrated glacial acetic acid solution with four times its weight of chromium trioxide dissolved in acetic acid, the mixture being kept at 15°–20° during 3 days (Miller, Ber. 1884, 17, Ref. 355). The product can be purified either by distillation with steam or by crystallisation from light petroleum (b.p. 85°–120°).

Identification.—It crystallises in yellow triclinic needles, m.p. 125°, begins to sublime below 100°, has the odour of *p*-benzoquinone, is readily volatile with steam, and dissolves easily in most organic solvents, but only sparingly in light petroleum or water.

Reactions.—It is not reduced by sulphurous acid in the cold, but by hydriodic acid and phosphorus or by tin and hydrochloric acid it is converted into 1 : 4-*dihydroxynaphthalene.* Partial reduction results in the formation of *naphthaquinhydrone.* Oxidation in caustic soda solution by atmospheric oxygen gives 2-*hydroxy-*[α-]*naphthaquinone*, but with nitric acid or permanganate furnishes *phthalic acid* (Liebermann and Dittler, Annalen, 1876, 183, 243; Japp and Miller, Chem. Soc. Trans. 1881, 39, 220; *cf.* Boswell, J. Physical Chem. 1907, 11, 119). In acetic acid solution with chlorine the *dichloride*, m.p. 176°, is formed and with bromine the *dibromide*, m.p. 92° (Zincke and Schmidt, Ber. 1894, 27, 2757).

With phenylhydrazine it yields the *hydrazone*, identical with benzeneazo-α-naphthol (Zincke and Bindewald, Ber. 1884, 17, 3026). With hydroxylamine it forms the *monoxime*, identical with 4-nitroso-α-naphthol (Goldschmidt and Schmid, *ibid.* 2064). With aniline in alcoholic solution 2-*anilino-*[α-]*naphthaquinone* is obtained. By acetic anhydride and zinc chloride or by sulphuric acid at 50° it is converted into the *triacetate* of 1 : 2 : 4-trihydroxynaphthalene.

(iii.) 2 : 6-**Naphthaquinone**, obtained from 2 : 6-dihydroxynaphthalene by oxidation in boiling benzene solution with lead peroxide, forms reddish-yellow prisms, and is odourless and non-volatile, but unlike [β-]naphthaquinone, is an oxidising agent comparable in this respect with *p*-benzoquinone (Willstatter and Parnas, Ber. 1907, 40, 1411, 3971).

Hydroxynaphthaquinones.

(i.) 2-**Hydroxy-**[α-]**naphthaquinone**[1] can be obtained by boiling amino-[α-]naphthaquinoneimide (diimino-α-naphthol, *v.* 2 : 4-diamino-α-naphthol) with dilute acids (Graebe and Ludwig, Annalen, 1870, 154, 321), or with sodium carbonate solution which afterwards is acidified (Diehl and Merz, Ber. 1878, 11, 1315); *or* by heating 2-anilino-[α-]naphthaquinone with hydrochloric acid (Baltzer, Ber. 1881, 14, 1900); *or* by dissolving [β-]naphthaquinone-4-sulphonic acid in sulphuric acid and, after some hours at 25°, pouring the solution on to ice (Aktienges., D. R.-P. 100703; Eng. P. 26675 of 1897). It is formed, also, when an alkaline solution of [α-]naphthaquinone (Kowalski, Ber. 1892, 25, 1659) or of 1 : 2-dihydroxynaphthalene-4-sulphonic acid (Bayer, D. R.-P. 70867; Eng. P. 825 of 1893) is exposed to the air; and readily by oxidizing either [β-]naphthaquinone, suspended in caustic soda solution, with hydrogen peroxide (Teichner and Weil, Ber. 1905, 38, 3376) or 1 . 2 : 4-trihydroxynaphthalene in aqueous solution with dichromate mixture at 0° (Thiele and Winter, Annalen, 1900, 311, 347).

Identification.—It crystallises or sublimes in yellow needles, m.p. 190°–191°, dissolves only sparingly in boiling water, expels carbon dioxide from carbonates, and dyes wool or silk yellow. The *acetate* forms yellow scales, m.p. 130° (Thiele and Winter, *l.c.*).

Reactions.—It couples with diazotised bases in presence of sodium acetate, forming *azo-* dyes which are remarkable because in them, the 1- or *α* position not being available, the azo- group has taken up the alternative *ortho*-, namely the 3- or *β*- position to the hydroxyl radicle (Kehrmann and Goldenberg, Ber. 1897, 30, 2126). On reduction with tin and hydrochloric acid, it yields 1 : 2 : 4-*trihydroxynaphthalene*.

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[1] By condensation with *o*-phenylenediamine, 2-hydroxy-[α-]naphthaquinone gives an *azine* (Kehrmann, Ber. 1890, 23, 2453), behaving as if it were 4-hydroxy-[β-]naphthaquinone. Many of the monosubstituted naphthaquinones of the 1 : 2 : 4-type exhibit a similar tautomerism (*cf.* Miller, Chem. Soc. Abstr. 1911, i. 465), although the formulæ usually assigned to them represent only one of the two isomeric forms.

3-Nitro-2-hydroxy-[*α*-]naphthaquinone is formed from [*β*-]naphthaquinone-4-sulphonic acid, or from 1-amino-2-naphthol-4-sulphonic acid by nitration in sulphuric acid solution below 50° (Aktienges., D. R.-P. 100611 ; Eng. P. 26675 of 1897). It is crystalline, and with phenylhydrazinesulphonic acid gives a yellow *azo*- dye for wool (Aktienges., D. R.-P. 102071 ; Eng. P. 676 of 1898).

2-Hydroxy-[*α*-]naphthaquinone-3-sulphonic acid, obtained by sulphonating 2-hydroxy-[*α*-]naphthaquinone with 25 p.c. anhydro- acid at 20°, forms a sparingly soluble *sodium* salt in pale yellow scales (Aktienges., D. R.-P. 99759 ; Eng. P. 26675 of 1897), and with phenylhydrazinesulphonic acid (Aktienges., D. R.-P. 101918 ; Eng. P. 676 of 1898) or with the hydrazine from 1-amino-8-naphthol-3 : 6-disulphonic acid (Aktienges., D. R.-P. 102070 ; Eng. P. 676 of 1898), gives respectively an orange-yellow or reddish-yellow *azo*-dye for wool.

The 6-sulphonic acid is produced when a mixture of [*β*-]naphthaquinone-4 : 6-disulphonic acid and sulphuric acid is kept at 25° for some hours (Aktienges., D. R.-P. 100703 ; Eng. P. 26675 of 1897) ; or when 1 : 2-dihydroxynaphthalene-6-sulphonic acid is oxidised in caustic soda solution with hydrogen peroxide (Teichner and Weil, Ber. 1905, 38, 3376). The *sodium* salt forms red needles.

The 7-sulphonic acid (Gaess, Ber. 1899, 32, 237), which gives two *sodium* salts $NaA+3H_2O$, and Na_2A, and two *barium* salts BaA_2+2H_2O, and $BaA+3\frac{1}{2}H_2O$, forms an *azine* with *o* phenylenediamine, reacting as if it were 4 hydroxy-[*β*-]naphthaquinone-7-sulphonic acid.[1]

(ii.) 5-**Hydroxy**-[*α*-]**naphthaquinone** (*juglone*; *regianin*; *nucin*) occurs in the green parts and shells of the walnut (Brissemoret and Combes, Compt. rend. 1905, 141, 838 ; Combes, Bull. Soc. chim. 1907, [iv.] 1, 803), but in nuts not freshly gathered is replaced in part or wholly by hydrojuglone (*cf.* Mylius, Ber. 1885, 18, 2567). It can be extracted from the shells by ether (Combes, *l.c.*), and is obtained by oxidation of 1 : 4 : 5 - trihydroxynaphthalene (hydrojuglone) with ferric chloride (Mylius, *l.c.*), or chromic acid (Bernthsen and Semper, Ber. 1885, 18, 204*7*; *or* of 1 : 5-dihydroxynaphthalene with chromic acid mixture (*ibid.* Ber. 1887, 20, 939 ; Willstätter and Wheeler, Ber. 1914, 47, 2798) ; *or* of 4 : 8-diamino-*α*-naphthol with ferric chloride (Friedländer and Silberstern, Monatsh, 1902, 23, 517).

Identification.—It crystallises in yellowish-red or brown needles, m.p. 151°–154°, is almost insoluble in water, and in aqueous solution colours the skin yellow like walnut juice. Its *tribromo*- derivative dyes silk and wool (Wheeler and Scott, J. Amer. Chem. Soc. 1919, 41, 835).

(iii.) 6-**Hydroxy**-[*β*-]**naphthaquinone**, prepared by oxidising 1-amino-2 : 6-dihydroxynaphthalene with ferric chloride, forms brick-red scales, decomp. at 165° (Kehrmann, Ber. 1907, 40, 1962).

The 4-sulphonic acid is obtained from 1-nitroso-2 : 6-dihydroxynaphthalene by interaction with sodium bisulphite solution and oxidation of the product (Bayer, D. R.-P. 87900 ; Eng. P. 6035 of 1893).

(iv.) 7-**Hydroxy**-[*β*-]**naphthaquinone**, obtained by oxidising 1-amino-2 : 7-dihydroxynaphthalene (Clausius, Ber. 1890, 23, 522), forms brown needles, m.p. 194° (Nietzki and Knapp, Ber. 1897, 30, 1123).

The 4-sulphonic acid, prepared by oxidising 1-amino-2 : 7-dihydroxynaphthalene-4-sulphonic acid with nitrous acid (Boniger, Ber. 1894, 27, 3051), gives a *potassium* salt in brown needles (Bayer, *l.c.*).

(v.) 8-**Hydroxy**-[*β*-]**naphthaquinone** has not been described. The 6-sulphonic acid, obtained by oxidising 8-hydroxy-1 : 2-diamino-naphthalene-6-sulphonic acid with dichromate, has been used like the foregoing isomerides for the production of *thiazines* (Bayer, *l.c.*).

(vi.) 2 : 3-**Dihydroxy**-[*α*-]**naphthaquinone** (Iso-*naphthazarin*) is formed when 3-amino-2-hydroxy-[*α*-]naphthaquinone is heated with dilute hydrochloric acid at 180° (Diehl and Merz, Ber. 1878, 11, 1322) ; *or* when 1 : 4-diamino-2 : 3-dihydroxynaphthalene is oxidised by ferric chloride (Friedlander and Silberstern, Monatsh. 1902, 23, 525) ; *or* when [*β*-]naphthaquinone is dissolved in dilute bleaching powder solution, which is then acidified with acetic acid and boiled with a few c.c. of hydrochloric acid (Zincke and Ossenbeck, Annalen, 1899, 307, 11 ; *cf.* Bamberger, Ber. 1892, 25, 134, 891 ; Zincke and Schartenberg, *ibid.* 409).

Identification.—It crystallises in red needles, m.p. 280° ; dissolves in caustic alkali solutions with a blue colour which disappears on exposure to the air, o-*carboxyphenylglyoxylic acid* being formed ; yields 1 : 2 : 3 : 4-*tetrahydroxynaphthalene* on careful, but 1 : 2 : 3-*trihydroxynaphthalene* on vigorous reduction with zinc and dilute sulphuric acid ; and is a dye for mordanted wool. Its *diacetate* forms colourless needles, m.p. 105° (Zincke and Ossenbeck, *l.c.*).

(vii.) 5 : 6 - **Dihydroxy** - [*α* -]**naphthaquinone** (**Naphthazarin** ; *Alizarin black*,) was first obtained by heating 1 : 5-dinitronaphthalene with zinc and sulphuric acid at 200° (Roussin, Compt. rend. 1861, 52, 1033, 1177 ; *cf.* Liebermann, Annalen, 1872, 162, 330). As it can be formed by boiling 1 : 4 : 5 : 6-tetra-aminonaphthalene with dilute hydrochloric acid, its constitution is known with certainty (Will, Ber. 1895, 28, 2234 ; Friedlander and Silberstern, Monatsh. 1902, 23, 518).

Preparation.—It is produced on the large scale by stirring 1 : 5-dinitronaphthalene (2 pts.) into monohydrate (40 pts.), adding a solution of sulphur (1 pt.) in 40 p.c. anhydro-acid (10 pts.) below 40°, and, when a test gives a blue solution, pouring the ‘ naphthazarin melt ’ into water, removing sulphur by filtration, and boiling the filtrate until the colour has changed to red (Bayer, D. R.-P. 71386). Substances which yield sulphur, such as hydrogen sulphide, sulphur chloride, &c., can replace it as reducing agents (Bayer, D. R.-P. 77330 ; Eng P. 17673 of 1892).

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[1] *See* footnote, p. 508.

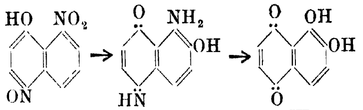
1 : 8-Dinitronaphthalene (1 pt.) also furnishes naphthazarin when dissolved in sulphuric acid (20 pts) and reduced at 120°–130° *either* with aniline, phenylhydrazine, tin or iron (Badische, D. R.-P. 76922; Eng. P. 3828 of 1894) *or* electrolytically (Badische, D. R.-P. 79406) provided the melt [1] is boiled with water; hence it is possible in the manufacturing process to substitute the dinitration product from naphthalene for the pure 1 : 5-dinitro-derivative.[2]

Properties.—It sublimes in brown needles showing a green lustre, is only sparingly soluble in water, but dissolves in alkalis forming a cornflower-blue, and in sulphuric acid a magenta solution. It is an important dyestuff, giving very fast violet-black lakes with chromium salts. When warmed at 50°–70° with sodium bisulphite solution, it is converted into a soluble compound used in dyeing under the name of alizarin black S and naphthazarin S (Badische, D. R.-P. 41518; Eng. P. 7833 of 1887), but with concentrated sodium bisulphite solution at 100°, followed by oxidation of the resulting leuco-compound, it yields *naphthazarinsulphonic acid* (Höchst, D. R.-P. 116866). The *diacetate*, needles, m.p. 189° (Zincke and Schmidt, Annalen, 1895, 286, 36), and the *tetra-acetate* of 1 : 2 : 5 : 8-tetrahydroxynaphthalene (Liebermann, Ber. 1895, 28, 1457) have been prepared from it.

By condensation of naphthazarin with salts of aromatic amines or with their sulphonic acids at 25°–40° in presence of boric acid, black dyes are formed (Badische, D. R.-P. 101525, 101152; Eng. P. 21297 of 1897; D. R.-P. 157684; Eng. P. 2468 of 1904).

Naphthazarin Melt.

Naphthazarin melt contains a 'naphthazarin intermediate product,' the blue solution of which in water, when boiled, gives naphthazarin. This 'intermediate product,' although its constitution has not been established by direct experiment, is probably an impure form of *5-amino-6-hydroxy-*[α-]*naphthaquinoneimide* [3] Consideration of the results recorded in the numerous patents of the Badische Anilin- u. Soda-Fabrik and other firms during the period 1896–1900 and of those arising from the investigations of Graebe and of Friedländer on the nitronitrosonaphthols (*q.v.*) separated from the naphthazarin melt has revealed a close resemblance between the naphthazarin reaction and that which takes place when 1 : 5-dinitroanthraquinone, anhydro- acid and sulphur are heated at 50°. The latter leads to the formation of a soluble, bluish-violet 'intermediate product,' identified as 1-nitro-5-nitroso-8-hydroxyanthraquinone (Bayer, D. R.-P. 104282; *cf.* 105567). By analogy, therefore, the course of the naphthazarin reaction may be represented by the formulæ:—



I II III

The 1-nitro-5-nitroso-8-hydroxynaphthalene or 8-nitro-4-nitroso-α-naphthol (I) is formed from 1 : 5-dinitronaphthalene at relatively low temperatures, but the 'intermediate product' (II) at higher temperatures, passing when boiled with dilute acids into naphthazarin (III.) with elimination of the NH_2 radicle as ammonia.

'Naphthazarin Intermediate Product,' and the derived colouring matters.

The **intermediate product** can be isolated by precipitating naphthazarin melt with zinc chloride (Hochst, D. R.-P. 111683; Eng. P. 16295 of 1899); *or* by oxidising the leuco-compound (*v. infra*), dissolved in caustic soda, with a rapid current of air (Badische, D. R.-P. 108551), or a solution of the melt with hypochlorite or dichromate (*ibid.*, D. R.-P. 101372; Eng. P. 15909 of 1898), and boiling the sodium salt thus obtained (which separates as blue needles) with acetic acid (*ibid.*, D. R.-P. 108552).

From naphthazarin melt, black, bluish-grey, green, or blue mordant dyes are obtained by oxidation with dichromate (Badische, D. R.-P. 101372; Eng. P. *l c.*); by condensation either with phenols (*ibid.*, D. R.-P. 103150; Eng. P. 10597 of 1898), or with aromatic amines (*ibid.*, D. R.-P. 118078; Eng. P. 20997 of 1899; Hochst, D. R.-P. 125574; Eng. P. 20485 of 1899); or by sulphonation with 20 p.c. anhydro-acid (Hochst, D. R.-P. 117359) respectively.

Reduction with stannous chloride converts naphthazarin melt into the **leuco**-compound, crystallising in colourless needles (Badische, D. R.-P. 101371, Eng. P. 15708 of 1898), which, sulphonated with 23 p.c. anhydro-acid, gives a blue dye (*ibid.*, D. R.-P. 106029; Eng. P. 24752 of 1898) convertible into black, green, or blue mordant dyes by boiling respectively with hydrochloric acid (*ibid*, D. R.-P. 106033; Eng. P. *l.c.*), or with aniline and aniline hydrochloride (*ibid.*, D. R.-P. 108414; Eng. P. *l.c.*), or with aniline hydrochloride and water (*ibid.*, D. R.-P. 108415).

(viii.) 6 : 7 - **Dihydroxy** - [*α* -]**naphthaquinone,** obtained from 5-amino-2 : 3 : 8-trihydroxynaphthalene by oxidation with ferric chloride, forms reddish-brown needles and has only feeble dyeing properties. Its *diacetate* forms yellow needles, m.p. 65°–67° (Friedländer and Silberstern, Monatsh. 1902, 23, 532).

(ix.) 5 : 6 : 8-**Trihydroxy**-[*α*-]**naphthaquinone** (*naphthapurpurin*), one of the products ('A') of the action of sulphuric acid in presence of boric acid on 1 : 5-dinitronaphthalene at 220° (Bayer, D. R.-P. 82574), is obtained in a pure state either by boiling naphthazarin with an equal weight of caustic soda in 1 p.c. solution until the colour has changed to magenta (Badische, D. R.-P. 167641; Eng. P. 9547 of 1905), or with manganese dioxide and dilute sulphuric acid (Jaubert, Compt. rend. 1899, 129, 684). It forms reddish-brown needles, is easily soluble in the ordinary solvents, dyes wool orange-red chroming to black (Badische, *l.c.*), and condenses with aromatic amines forming dyes, which when sulphonated give blue, green, or black shades on chromed wool (Bayer, D. R.-P. 127766).

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[1] The naphthazarin melt from 1 : 8-dinitronaphthalene contains an intermediate product different from, but probably isomeric with, that furnished by 1 : 5-dinitronaphthalene.

[2] When heated in sulphuric acid solution at 130° with hydrogen sulphide, 1 : 5-dinitronaphthalene (Badische, D. R.-P. 134705; Eng. P. 6053 of 1900; Höchst, D. R.-P. 138105), and 1 : 8-dinitronaphthalene (Badische, D. R.-P. 114264; Eng. P. 890 of 1900) give products which, unlike naphthazarin, develop blue and violet shades on wool without a mordant.

[3] According to Agular and Bayer, the melt contains in addition a trihydroxy-[α-]naphthaquinone, obtainable also by heating naphthazarin with sulphuric acid (Ber. 1871, 4, 439).

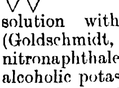
NAPHTHAQUINONESULPHONIC ACIDS.

[*β*-]**Naphthaquinone-4-sulphonic acid**, prepared by oxidising 2-amino-1-naphthol-4-sulphonic acid (Witt and Kaufmann, Ber. 1891, 24, 3163), or 1-amino-2-naphthol-4-sulphonic acid (Böniger, Ber. 1894, 27, 24) with nitric acid; *or* 1 : 2-dihydroxynaphthalene-4-sulphonic acid with nitrous acid (Bayer, D. R.-P. 83046; Eng. P. 825 of 1893), forms easily soluble salts.

Reactions.—It is converted by nitrosulphuric acid into 3-*nitro-2-hydroxy-*[α-]*naphthaquinone*, or by sulphuric acid at 25° into 2-*hydroxy*-[α-] *naphthaquinone*; is reduced to 1 : 2-*dihydroxynaphthalene*-4-*sulphonic acid* by sulphurous acid; and gives *thiazines* by condensation with aromatic nitroso- compounds (Bayer, *l c.*), also *oxazines* with aminonaphtholsulphonic acids (Dahl, D. R.-P. 82740; Eng. P. 5153 of 1895).

By oxidising the corresponding aminonaphtholsulphonic acids, the [*β*-]naphthaquinone-6-, 7-, and 8-mono-, and 4 : 6-, 4 : 7-, 4 : 8-, and 6 : 8-di-sulphonic acids have been obtained, which furnish *thiazines* by condensation with aromatic nitroso-compounds (Bayer, D. R.-P. 84233; Eng. P. 4757 of 1893; *cf.* Boniger, *l.c.* 3052).

NAPHTHAQUINONEOXIMES.



(i.) 2-**Nitroso-α-naphthol** ([*β*-] *naphthaquinone-2-oxime*) can be obtained from [*β*-]naphthaquinone by boiling it in alcoholic solution with hydroxylamine hydrochloride (Goldschmidt, Ber. 1884, 17, 215); *or* from *β*-nitronaphthalene by warming it with methyl alcoholic potash (Meisenheimer and Witte, Ber. 1903, 36, 4167); *or* from 1-hydroxy-*β*-naphthoic acid by means of nitrous acid (Reverdin and de la Harpe, Ber. 1893, 26, 1280); *or*, mixed with the 4-oxime (*q.v.*), from α-naphthol by interaction with nitrous acid (Fuchs, Ber. 1875, 8, 626; Worms, Ber. 1882, 15, 1816; Ilinski, Ber. 1884, 17, 2589; Henriques and Ilinski, Ber. 1885, 18, 706). It crystallises in yellow needles, m.p. 152° (Goldschmidt, *l.c.*), soluble in the ordinary organic solvents or in hot water; forms coloured salts and ethers, the *potassium* and *ammonium* salts being green, and the *methyl* (m.p. 95°) and *ethyl* (m.p. 101°) *ethers* greenish-yellow (Fuchs, *l c.*).

Reactions.—Concentrated nitric acid in acetic acid solution converts it into 2 : 4-*dinitro-α-naphthol*; potassium ferricyanide in alkaline solution oxidises it rapidly to 2-*nitro-α-naphthol*. With sodium bisulphite solution it yields 2-*amino*-1-*naphthol-4-sulphonic acid*. Like nitroso *β*-naphthol it gives [*β*-]*naphthaquinonedioxime* with hydroxylamine (Goldschmidt and Schmid, Ber. 1884, 17, 2066), forms metallic salts (Ilinski, *ibid.* 2592), and is a mordant dye (*cf.* Aktienges., D. R.-P. 66786).

2-Nitroso-1 : 8-dihydroxynaphthalene (Erdmann, Annalen, 1888, 247, 358) gives black lakes (Bayer, D. R.-P. 51478; Eng. P. 14230 of 1889).

2-Nitroso-α-naphthol-4-sulphonic acid gives a *naphthol green* with ferric chloride (Gans & Co., D. R.-P. 28065; Eng. P. 2269 of 1884; Hoffmann, Ber. 1885, 18, 46).

(ii.) 4-**Nitroso-α-naphthol** ([α-]*naphthaquinone-4-oxime*) is formed when [α-]naphthaquinone in alcoholic solution is boiled with hydroxylamine hydrochloride (Goldschmidt and Schmid, Ber. 1884, 17, 2064), *or*, mixed with the 2-oxime (*q.v.*) by the interaction of α-naphthol with nitrous acid. The best yield, *viz.* 40 grms. of the colourless 4-oxime and 50 grms. of the yellow 2-oxime from 100 grms. of α-naphthol, is obtained by boiling a solution of α-naphthol (1 pt.) and zinc chloride (1 pt.) in alcohol (6 pts.) with aqueous sodium nitrite (0·5 pt.) during 2-3 hours, the product which separates consisting of the 4-oxime mixed with the zinc salt of the 2-oxime (Henriques and Ilinski, Ber. 1885, 18, 706; *cf.* Ilinski, Ber. 1884, 17, 2590). It crystallises in needles, m.p. 190° (Friedländer and Reinhardt, Ber. 1394, 27, 240), dissolves easily in alcohol or ether, gives a *methyl ether*, m.p. 98°-100° (Ilinski, *l.c.*), and is destitute of tinctorial power (Kostanecki, Ber. 1887, 20, 3147).

Reactions.—Concentrated nitric acid in acetic acid solution converts it into 2:4-*dinitro-α-naphthol*; potassium ferricyanide in alkaline solution oxidises it very slowly to 4-*nitro-α-naphthol.* Reduction with stannous chloride furnishes 1-*amino-4-naphthol.* Like the 2-oxime and [*β*-]naphthaquinone-1-oxime, it gives 2-*anilino*-[α-]*naphthaquinoneanil*, m.p. 187°, when boiled with aniline and acetic acid (Brömme, Ber. 1888, 21, 393).

4-Nitroso-α-naphthol-2-sulphonic acid is readily converted into 2 : 4-*dinitro-α-naphthol* by dilute nitric acid (Conrad and Fischer, Annalen, 1893, 273, 110).

4-Nitroso-α-naphthol-2 : 5-disulphonic acid is formed when α-nitronaphthalene-3 : 8-disulphonic acid is warmed with concentrated caustic soda solution. Its *potassium* salt, $K_2A+1\frac{1}{2}H_2O$, forms yellow, and *basic potassium* salt green, needles; the *amino*-acid, obtained from it by reduction, furnishes 1-*amino*-4-*naphthol* on desulphonation with sodium amalgam (Friedlander, Ber. 1895, 28, 1535).

5-**Nitro-4-nitroso-α-naphthol** (5-*nitro*-[α-] *naphthaquinoneoxime*) is produced when 1 : 8-dinitronaphthalene is heated with 12–23 p.c. anhydro-acid at 40°–50° (Badische, D. R.-P. 90414; Eng. P. 14955 of 1896; Graebe, Ber. 1899, 32, 2877; Friedländer, *ibid.* 3528; Friedländer and Scherzer, *cf.* J. Soc. Chem. Ind. 1900, 19, 339). It crystallises in yellow needles, and is soluble in alkalis giving yellow solutions which become red when heated with zinc dust (Badische, *l.c.*).

Reactions.—By potassium ferricyanide it is oxidised to 4 : 5-*dinitro-α-naphthol*; by dilute nitric acid to 2 : 4 : 5-*trinitro-α-naphthol* and by permanganate to 3-*nitrophthalic acid.* When reduced with ammonium sulphide or stannous chloride, it gives 4 : 5-*diamino-α-naphthol*, but with tin and hydrochloric acid 5-*amino*-1 : 4-*dihydroxynaphthalene*.

The 2 : 7-disulphonic acid, formed by the action of very dilute caustic soda solution [1] on

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[1] If concentrated caustic soda solution is used, the product is a 1 : 8-dinitrosodihydroxynaphthalene-3 : 6-disulphonic acid, the *sodium* salt Na_3A+3H_2O of which crystallises in needles (Kalle, *l.c.*).

1 : 8-dinitronaphthalene-3 : 6-disulphonic acid at the ordinary temperature, gives a yellow *potassium* salt K_2A+2H_2O and a green *basic potassium* salt. With dilute nitric acid it furnishes a crystalline yellow *nitro-* dye with the loss of one of the SO_3H groups (Kalle, D. R.-P. 113063).

7-**Nitro-4-nitroso-α-naphthol** (7-*nitro*-[α-] *naphthaquinone*-4-*oxime*), obtained when 1 : 6-dinitronaphthalene is heated with 15–17 p.c. anhydro-acid at 40°–50°, crystallises in yellow needles, is soluble in alkalis, and on oxidation gives 4-*nitrophthalic acid* (Graebe, Annalen, 1904, 335, 144).

8-**Nitro-4-nitroso-α-naphthol** (8-*nitro*-[α-] *naphthaquinone*-4-*oxime*), obtained by heating 1 : 5-dinitronaphthalene with 12–23 p.c. anhydro-acid at 40°–50° (Badische, D. R.-P. 91391 ; Eng. P. 14955 of 1896 ; *v.* 5-nitro- compound for other references) forms yellow crystals; these dissolve in alkalis giving yellow solutions, which become green when boiled with zinc dust (Badische, *l.c.*).

Reactions.—By potassium ferricyanide it is converted into 4 : 8-*dinitro-α-naphthol*, but by dilute nitric acid into 2 . 4 : 8-*trinitro-α-naphthol.* When reduced with tin and hydrochloric acid, it furnishes 1 : 5-*diamino-8-naphthol.*

(iii.) 1-**Nitroso-β-naphthol** ([β-]*naphthaquinone*-1-*oxime*) is obtained by the action of nitrous acid on β-naphthol (Fuchs, Ber. 1875, 8, 1026 ; Ilinski, Ber. 1884, 17, 2584 ; Groves, Chem. Soc. Trans. 1884, 45, 295 ; *cf.* Köhler, D. R.-P. 25469).

Preparation.—Sodium nitrite (2 pts.) in solution is added to a hot solution of β-naphthol (4 pts.) and zinc chloride (3 pts.) in alcohol (24 pts.), the mixture boiled for a short time and the sparingly soluble reddish-brown zinc salt which separates freed from zinc by digestion with caustic soda solution in the cold, the oxime being precipitated from the filtrate by acidification (Henriques and Ilinski, Ber. 1885, 18 705 ; Paul, Z. angew. Chem. 1897, 10, 47). *Or,* as a greenish-yellow precipitate, it is produced when 10 p.c. sulphuric acid (700 c.c.) is added gradually to a solution of β-naphthol (50 grms.), caustic soda (14 grms.), and sodium nitrite (25 grms.) in water (1500 c.c.) containing one-third its weight of ice (Lagodzinski and Hardine, Ber. 1894, 27, 3076).

Identification.—It crystallises from alcohol in anhydrous orange-brown thin plates or short thick prisms, m.p. 109·5°, dissolves only very sparingly in hot water, and when pure is readily volatile with steam (Ilinski, *l.c.*). The *cupric* salt CuA_2 (Knorre, Ber. 1887, 20, 283), and *ferric* salt FeA_3, are insoluble in water or in 50 p.c. acetic acid, and the *cobaltic* salt CoA_3, is only very slightly soluble in boiling 50 p.c. acetic acid (Ilinski and Knorre, Ber. 1885, 18, 699 ; 2728). Since Hg, Pb, Cd, Al, Cr, Ni, Zn, Mn, Mg, Gl, &c., are not precipitated by it in acetic acid solution, nitroso-β-naphthol can be employed for the quantitative separation of Cu, or Fe, or Co, from any of the metals named (*cf.* Knorre, Z. angew. Chem. 1893, 6, 264 ; Atack, J. Soc. Chem. Ind. 1915, 34, 641). The *barium, potassium* KA, and *sodium* salts are green (Ilinski, Ber. 1884, 17, 2885).

Reactions.—By dilute nitric acid or potassium ferricyanide it is converted into 1-*nitro-β-naphthol.* When reduced with stannous chloride, 1-*amino-β-naphthol* is obtained. Dissolved in cold caustic soda solution, it yields [β-]*naphthaquinonedioxime*, m.p. 180°–181°, with hydroxylamine, but if the alkali solution be warm the *anhydride*, m.p. 78°, is the product (Kehrmann and Messinger, Ber. 1890, 23, 2815). By concentrated sodium bisulphite solution below 50°, it is converted into a crystalline bisulphite *compound*, which, unlike nitroso-β-naphthol, couples with diazotised bases forming *azo-* dyes (Dahl, D. R.-P. 79583 ; 95758 ; *cf.* Ashworth and Bürger, Eng. P. 11556 of 1893). When decomposed by hydrochloric acid this compound furnishes 1-*amino-2-naphthol-4-sulphonic acid* (Boniger, Ber. 1894, 27, 23).

Under the name 'Gambin R,' it has been introduced as a mordant dye for cotton (Aktienges., D. R.-P. 66786).

1-Nitroso-β-naphthol-6-sulphonic acid, formed by the action of nitrous acid on β-naphthol-6-sulphonic acid (Meldola, Chem. Soc. Trans. 1881, 39, 40), gives a *barium* salt BaA_2+H_2O, in orange needles; a green *basic barium* salt $BaA+H_2O$; a *basic sodium* salt Na_2A+2H_2O, in green needles (Hoffmann, Ber. 1891, 24, 3471), and coloured metallic salts with Co, Ni, and Fe, from which the metal is not precipitated by alkalis or alkali carbonates. With ferric chloride and sodium carbonate it forms the *iron sodium salt* $Fe(NaA)_3$ (Gans, D. R.-P. 28065 ; Eng. P. 2269 of 1884 ; Hoffmann, Ber. 1885, 18, 46 ; *l.c.*), which, under the name *naphthol green*, has been introduced as a green dye for wool (Gans, D. R.-P. 28901 ; *cf.* Ulrich, J. Soc. Chem. Ind 1890, 9, 1126).

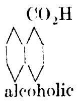
The 3 : 6-disulphonic acid, obtained similarly from β-naphthol-3 : 6-disulphonic acid, gives a *sodium* salt in golden yellow fan-like crystals, 2·6 grms. of which dissolve in 100 grms. water at 18°. This salt is used as a sensitive test for cobalt, as by its aid 0·5 p.c. of cobalt can be detected in nickel (Van Klooster, J. Amer. Chem. Soc. 1921, 43, 746).

1-Nitroso-2 : 6-dihydroxynaphthalene (Bayer, D. R.-P. 55126 ; 59268 ; Eng. P. 14230 of 1889) ; 1-nitroso-2 : 7-dihydroxynaphthalene or *dioxin* (Leonhardt, D. R.-P. 55204 ; Eng. P. 17223 of 1889) ; and nitroso-2 : 8-dihydroxynaphthalene (Bayer, D. R.-P. 53915 ; Eng. P. 14230 of 1889) are mordant dyes, the two former giving green shades with iron salts.

X. Carboxy- Derivatives.

The naphthoic acids are technically unimportant, as are their derivatives with the exception of the hydroxynaphthoic acids.

Naphthoic Acids.



α-**Naphthoic acid** can be prepared by heating α-naphthonitrile with hydrochloric acid at 200° (Boessneck, Ber. 1883, 16, 639), or with 15 p.c. alcoholic soda at 160° (Bamberger and Philip, Ber. 1887, 20, 242), but most easily by boiling it with a mixture of sulphuric and acetic acids (Rabe, Ber. 1898, 31, 1898). It is also formed when α-bromonaphthalene is heated with aqueous potassium cyanide and a small quantity of cuprous cyanide at 200° under pressure (Rosenmund and Struck, Ber. 1919, 52, 1755). It crystallises in needles, m.p. 160°, b.p. 300°, dissolves only sparingly in hot water, and on nitration yields both the 5-*nitro*- and the 8-*nitro-α-naphthoic acids* (Ekstrand, J. pr. Chem. 1888, [ii.] 38, 156). The *barium* salt BaA_2+4H_2O, and the *calcium* salt CaA_2+2H_2O, crystallise in needles; the *nitrile* in needles, m.p. 34°, b.p. 299°.

β-**Naphthoic acid** is obtained when β-naphthonitrile is boiled with alcoholic potash (Vieth, Annalen, 1876, 180, 305), or with a mixture of sulphuric and acetic acids (Baeyer and Besemfelder, Annalen, 1891, 266, 187). It crystallises in silky needles, m.p. 184°, dissolves only sparingly in hot water, and yields *trimellitic acid* on oxidation with alkaline permanganate (Ekstrand, J. pr. Chem. 1891, [ii.] 43, 427). The *barium* salt BaA_2+4H_2O, and *calcium* salt CaA_2+3H_2O, crystallise in very sparingly soluble needles; the *nitrile* forms scales, m.p. 66·5°, b.p. 306·5°.

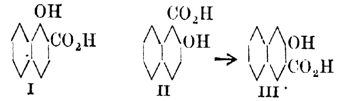
HYDROXYNAPHTHOIC ACIDS.

Introductory.—Two general methods have been used for the production of hydroxynaphthoic acids—

(1) Fusion of sulphonated naphthoic acids with caustic alkali;

(2) Interaction of the sodium salts of naphthols or dihydroxynaphthalenes with carbon dioxide under pressure at a suitable temperature.

The acids formed from the naphthols are—



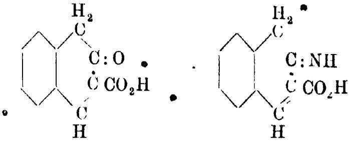
The α-acid (II) from β-naphthol is obtained at 120°-140°, and the β-acid (III) at 200°-250°, a transformation which affords one of the rare examples in the naphthalene series of the entry of a radicle into the 3- position to produce a 2 : 3- di-substitution derivative.

The order of stability of the three monohydroxy-acids may be inferred from the following facts:

(i.) Acid II, when heated alone or with water, loses carbon dioxide more readily than acid I; both acids by coupling furnish azo- dyes which do not contain the carboxyl group; and acid I with nitrous acid gives 2-nitroso-α-naphthol by elimination of the carboxyl group.

(ii.) Acid III, on the contrary, does not suffer these decompositions and loses carbon dioxide only when boiled with solutions of sodium bisulphite, ammonium bisulphite, or phenylhydrazine and bisulphite, furnishing β-naphthol, β-naphthylamine, and naphthacarbazole respectively (Bucherer, J. pr. Chem. 1905, [ii.] 71, 445; Bucherer and Seyde, D. R.-P. 208960; J. pr. Chem. 1908, [ii.] 75, 403).

2-Hydroxy-3-naphthoic acid and its derivatives are used as developers in the production of azo- dyes. They are remarkable as furnishing two series of compounds, one yellow and the other colourless. Thus the esters, amides, normal salts, &c. of this acid, of di- and trihydroxy- acids containing one of the hydroxyl groups relatively in the 2- position, and of 2-amino-3-naphthoic acid are yellow, whereas the 2-acetyl derivatives and basic salts are colourless. This difference in properties is referred by Möhlau to keto-enolic isomerism, the following formulæ being assigned to the yellow forms:



(Ber. 1895, 28, 3100).

(i.) 2-**Hydroxy-1-naphthoic acid** is obtained by acting on dry sodium β-naphtholate with solid, liquid, or gaseous carbon dioxide under pressure in the cold, and subsequently heating the sodium β-naphthyl carbonate thus produced at 120°-140° (Schmitt, D. R.-P. 31240; Schmitt and Burkard, Ber. 1887, 20, 2701; Heyden, D. R.-P. 38052). The *acid* crystallises in needles, m.p. 156°-157°, but when slowly heated begins to decompose at 124°-128°, and is converted quantitatively into β-naphthol and carbon dioxide by prolonged boiling with water (Schmitt and Burkard, *l.c.*). With ferric chloride a deep violet-black colouration is formed. It couples with diazotised bases, but the products are *azo*- derivatives of β-naphthol (Nietzki and Guitermann, Ber. 1887, 20, 1275).

The 6-sulphonic acid is formed from 2-hydroxy-1-naphthoic acid by sulphonation with 20 p.c. anhydro- acid at 40° (Seidler, D. R.-P. 53343), and its *chloride* by interaction with chlorosulphonic acid in the cold (Bayer, D. R.-P. 278091). It loses carbon dioxide forming *β-naphthol-6-sulphonic acid*, either when warmed in aqueous solution at 60°, or when coupled with diazotised bases (Seidler, *l.c.*).

(ii.) 8-**Hydroxy-1-naphthoic acid**, formed, together with the *anhydride* or lactone (m.p. 108°), by boiling diazotised α-naphthylamine-8-carboxylic acid with dilute sulphuric acid, crystallises in needles, m.p. 169° (Ekstrand, Ber. 1886, 19, 1138); it does not readily regenerate the lactone.

(iii.) 1-**Hydroxy-2-naphthoic acid** is obtained by acting on dry sodium α-naphtholate with carbon dioxide under pressure at 120°-145° (Heyden, D. R.-P. 38052), or with solid, liquid, or gaseous carbon dioxide in the cold and subsequently heating the sodium α-naphthyl carbonate thus produced at 120°-140° (Schmitt, D. R.-P. 31240; Schmitt and Burkard, Ber. 1887, 20, 2699). The *acid* crystallises in needles, m.p. 187°, is only very sparingly soluble in water (0·058 grm. in 100 c.c. at 17°), and gives with ferric chloride an intense blue colouration. The *sodium* salt $NaA+H_2O$, scales, and the *ammonium* salt NH_4A, needles, are readily soluble in hot water (Schmitt and Burkard, *l.c.*).

Reactions.—Nitrous acid reacts with it, forming 2-*nitroso-α-naphthol* with the elimination of carbon dioxide; nitric acid converts it into 2 : 4-*dinitro-α-naphthol* (Nietzki and Guitermann, Ber. 1887, 20, 1275). Chlorinated in acetic acid solution, it yields 4-*chloro*-1-*hydroxy*-2-*naphthoic acid*, from which carbon dioxide is readily eliminated and 4-*chloro-α-naphthol* obtained

(Kalle, D. P. Anm. K. 45914). With diazotised nitranilines it couples forming para-*azo-* dyes (Nietzki and Guitermann, *l.c.*; *cf.* Nietzki, D. R.-P. 44170; 46203; Eng. P. 17583 of 1887).

The 4-sulphonic acid is obtained from 1-hydroxy-2-naphthoic acid by warming it with monohydrate at 60°-70° until sulphonation is complete (Dahl, D. R.-P. 51715; *cf.* Konig, Ber. 1889, 22, 787) and its *chloride*, m.p. 200°, by interaction with chlorosulphonic acid in the cold (Bayer, D. R.-P. 264786; Eng. P. 18430 of 1913). The *acid* H_2A+5H_2O, crystallising in small needles, shows blue fluorescence in alkaline solution.

Reactions.—Nitric acid converts it successively into 4-*nitro*-1-*hydroxy*-2-*naphthoic acid* and 2:4-*dinitro*-α-*naphthol* (Konig, Ber 1890, 23, 806). With diazotised bases it interacts, but owing to elimination of carbon dioxide, the *azo-* dyes formed are derivatives of α-naphthol-4-sulphonic acid (Konig, *l.c.*; *cf.* Dahl, *l.c.*).

The 4:7-disulphonic acid is the main product of the sulphonation of 1-hydroxy-β-naphthoic acid with 20 p.c. anhydro-acid at 100° (Konig, Ber. 1889, 22, 787; Seidler, D. R.-P. 56328). The *acid* H_3A+4H_2O, needles, shows bluish-green fluorescence in alkaline solution (Konig, *l.c.*).

Reactions.—When boiled with 3 p.c. hydrochloric acid it yields α-*naphthol*-4:7-*disulphonic acid*, but with dilute sulphuric acid at 140° it gives 7-*sulpho*-1-*hydroxy*-2-*naphthoic acid* (Friedlander and Taussig, Ber. 1897, 30, 1460). Fusion with caustic alkali at 220°-240° converts it into 4-*sulpho*-1:7-*dihydroxy*-2-*naphthoic acid*, and at a higher temperature into 1:7-*dihydroxynaphthalene*-4-*sulphonic acid*. With diazotised bases it interacts forming *azo-* dyes of α-naphthol-4:7-disulphonic acid, owing to elimination of carbon dioxide (König, Ber. 1890, 23, 810).

(iv.) 2-**Hydroxy-3-naphthoic acid** is obtained by allowing the calculated quantity of carbon dioxide to act on dry sodium β-naphtholate at 200°-250° under pressure (Heyden, D. R.-P. 50341; Eng. P. 9612 of 1889; Schmitt and Burkard, Ber. 1887, 20, 2702) and purified by extracting the crude product with 5 p.c. sodium carbonate solution, neutralising the filtrate with hydrochloric acid, boiling it with animal charcoal, and when cold adding excess of acid to the filtrate (Strohbach, Ber. 1901, 34, 4142).

Identification.—It crystallises in yellow scales, m.p. 216°, dissolves only very sparingly in hot water, and is characterised by its great stability. Its normal salts; *ethyl* ester, needles, m.p. 85°, b.p. 290°-291° (Rosenberg, Ber. 1892, 25, 3634) and *hydrazide*, plates, m.p. 203°-204° (Franzen and Eichler, J. pr. Chem. 1908, [ii.] 78, 164) are yellow, but the *basic sodium* salt; the O-*acetyl* derivative, needles, m.p. 176°-177° (Grädenwitz, Ber. 1894, 27, 2624), the *amide*, m.p. 185° (Rosenberg, *l.c.*); the *anilide*, scales, m.p. 243°-244° (Schöpff, Ber. 1892, 25, 2743) and arylated amides generally (Griesheim, D. R.-P. 293897) are colourless, although the arylamides dissolve in alkalis giving yellow solutions.

Reactions.—On oxidation with potassium permanganate in alkaline solution it gives o-*carboxyphenylglyoxylic acid* (Schöpff, Ber. 1893, 26, 1123) and *phthalic acid* (Schmitt, *ibid.* 1114). With nitrous acid it yields 1-*nitroso*-2-*hydroxy*-3-*naphthoic acid* (Kostanecki, Ber. 1893, 26, 2898). By ammonia at 260°-280° it is converted into 2-*amino*-3-*naphthoic acid* (Möhlau, Ber. 1895, 28, 3096). Monohydrate at 60° gives a mixture of the 6- and 8-*sulphonic acids*, but chlorosulphonic acid in the cold the 1-*sulphonyl chloride*, m.p. 219° (Bayer, D. R.-P. 264786; Eng. P. 18430 of 1913). With diazotised bases it couples forming *azo-* dyes, without elimination of the carboxyl group (Kostanecki, *l.c.*; *cf.* Aktienges., D. R.-P. 77286; Eng. P. 15789 of 1892; Sircar and Watson, J. Soc. Chem. Ind. 1913, 32, 642).

Arylamides are obtained either by warming a suspension of 2-hydroxy-3-naphthoic acid and excess of the respective base with phosphorus trichloride, thionyl chloride, &c. (*cf.* Bayer, D. R.-P. 284997; 291712; Griesheim, D. R.-P. 264527; 291139; 293897; 295767; Eng. P. 13237; 23732 of 1913; 5444 of 1915; Hochst, D. R.-P. 294799), or by heating an O-acyl derivative of the acid at 200°-250° to constant weight and allowing the product to interact with the respective arylamine (*cf.* Hochst, D. R.-P. 289027; 294780, 295183). The anilide was first used as a source of azo- dyes by being coupled with diazotised primuline (Badische, D. R.-P. 221481), but later, under the name 'Naphthol A S,' was introduced as a developer for brilliant shades on the fibre, replacing β-naphthol, and it is in this direction that these arylamides have assumed importance.

The 1-amino-derivative has not been described, but the 1-*diazo-oxide*, and the *nitro*-compound, yellow needles puffing at 212°-213°, obtained by nitrating it, have been used to furnish dyes for chroming (Bindsch., D. R.-P. 206698).

The 6-sulphonic acid (L-*acid*), and the 8-sulphonic acid (S-*acid*), obtained by sulphonating 2-hydroxy-3-naphthoic acid with monohydrate at 60° or above, are separated as calcium salts, that of the L-acid being the more soluble in hot water (Gesellsch., D. R.-P. 69357; Schmid, Ber. 1893, 26, 1118; Hirsch, *ibid.* 1177), or as acid sodium salts, that of the L-acid being the less soluble (Bucherer, *cf.* J. Soc. Chem. Ind. 1903, 22, 945). The L-acid couples readily, but the S-acid only slowly with diazotised bases.

The 6:8-disulphonic acid is the chief product of the sulphonation of 2-hydroxy-3-naphthoic acid (Gesellsch., D. R.-P. 67000; Eng. P. 14161 of 1892), or of L- acid or S- acid (Schmid, *l.c.*), with 24 p.c. anhydro-acid at 125°-150°.

Reactions.—Fusion with caustic soda at 210°-240° converts it into 3-*sulpho*-1:7-*dihydroxy*-6-*naphthoic acid* (Gesellsch., *l.c.*; *cf.* D. R.-P. 71202; Schmid, *l.c.*). With ammonia solution at 240°-280°, it gives 6-*sulpho*-2-*amino*-8-*hydroxy*-3-*naphthoic acid* (Gesellsch., D. R.-P. 69740).

Of the remaining hydroxynaphthoic acids four have been obtained by fusing the isomeric sulphonaphthoic acids with caustic potash (Battershall, Annalen, 1873, 168, 121; Stumpf, Annalen, 1877, 188, 1), and two from the corresponding naphthylaminecarboxylic acids (Friedländer, Heilpern and Spielfogel, *cf.* J. Soc. Chem. Ind. 1898, 17, 836).

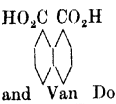
DIHYDROXYNAPHTHALENECARBOXYLIC ACIDS.

Introductory.—The dihydroxynaphthalenecarboxylic acids have little technical importance. *Five*, namely those containing the radicles OH : OH : CO_2H in the 1 : 2 : 3-, 1 : 4 : 2-, 1 : 7 : (?)-, 1 : 8 : 2-, and 2 : 7 : (3)- positions, have been obtained by interaction of the heated sodium salts of the respective dihydroxynaphthalenes with carbon dioxide under pressure (*cf.* Möhlau, Ber. 1893, 26, 3067; 1895, 28, 3093; Schmid, Ber. 1893, 26. 1117; Heyden, D. R.-P. 55414), and *two* containing these radicles respectively in the 1 : 7 : 6- (*infra*) and 2 : 6 : 3- positions, by fusion of the isomeric sulpho-2-hydroxy-3-naphthoic acids, S- and L-, with caustic alkali (*cf.* Schmid, *l.c.*; Gesellsch., D. R.-P. 69357). Of these acids four, *viz.* the 1 : 7 : 6-, 1 : 8 : 2-, 2 : 6 : 3-, and 2 : 7 : (3)-derivatives, couple with diazotised bases forming *azo-* dyes.

1 : 7-*Dihydroxynaphthalene-2-carboxylic acid.* The 4-sulphonic acid is produced by fusing 4 : 7-disulpho-1-hydroxy-2-naphthoic acid with 80 p.c. caustic soda solution at 190° (Bindsch., D. R.-P. 84653; Eng. P. 4620 of 1894), or with caustic soda at 220°–240° (Friedlander and Zinberg, Ber. 1896, 29, 38). It couples with diazotised bases (Bindsch., *l.c.*), and is converted into 1 : 7-*dihydroxynaphthalene-4 sulphonic acid* when heated with 30 p.c. caustic soda at 140°–160° (Bindsch., D. R.-P. 83965), but into the 2-*carboxylic acid* when either boiled with 20 p.c. hydrochloric acid (Bayer, D. R.-P. 89539), or heated at 140° with 50 p.c. sulphuric acid (Friedländer and Zinberg, *l.c.*).

1 : 7-*Dihydroxynaphthalene-6-carboxylic acid.* The 3-sulphonic acid (**nigrotic acid,** *cf.* Bucherer, J. pr. Chem. 1907, [ii.] 75, 287), obtained by fusing 6 : 8-disulpho-2-hydroxy-3-naphthoic acid with caustic soda at 210°–240° (Gesellsch., D. R.-P. 67000; Eng. P. 14161 of 1892; Schmid, Ber. 1893, 26, 1119) shows yellowish-green fluorescence in alkaline solution. It couples with diazotised bases forming black or grey *azo-* dyes (Gesellsch., D. R.-P. 71202; 75258; 80912; 84546; Eng. P. 14253 of 1892; 4460 of 1894).

NAPHTHALENEDICARBOXYLIC ACIDS.



Naphthalene-1 : 8-dicarboxylic acid (*naphthalic acid*), obtained by the oxidation of acenaphthene with chromic acid mixture (Behr and Van Dorp, Annalen, 1874, 172. 266; Anselm, Ber. 1892, 25, 652) is of interest on account of the readiness with which, like *ortho*-dicarboxylic acids, it is converted into an *anhydride* (m.p. 274°) and an *imino*- derivative (m.p. 300°); and of the resemblance which this *peri*- anhydride shows to phthalic anhydride in forming a *fluorescein* by condensation with resorcinol (Terisse, Annalen, 1885, 227, 135). The *diethyl* ester, which cannot be prepared by direct esterification, forms plates, m.p. 59°–60°; b.p. 238°–239° under 19 mm. (Wislicenus and Penndorf, Ber. 1912, 45, 410). From the imino-derivative, vat dyes have been obtained (Kardos, D. R.-P. 276357; 276358; Eng. P. 26690 of 1913). W. P. W.

NAPHTHAQUINONE *v* this vol., p. 507.

NAPHTHASE *v.* AZINES.

NAPHTHAZARIN *v.* this vol., p. 509.

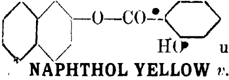
NAPHTHAZINES *v.* AZINES.

NAPHTHIONIC RED or **ARCHIL SUBSTITUTE** *v.* AZO- COLOURING MATTERS.

NAPHTHOL BLACK *v.* AZO- COLOURING MATTERS.

NAPHTHOL GREEN *v.* this vol., p. 512.

NAPHTHOLSALOL. Trade name for β-naphthol salicylate



used as an antiseptic.

NAPHTHOL YELLOW *v.* this vol., p. 474.

NAPHTHOPHENAZINE *v.* AZINES.

NAPHTHYLHYDRAZINE *v.* HYDRAZINES.

NAPHTHYLHYDRAZONES *v.* HYDRAZONES.

NAPLES YELLOW *v.* ANTIMONY.

NARCENE. *See* under MORPHINE.

NARCEÏNE *v.* OPIUM.

NARCISSINE $C_{16}H_{17}O_4N$. Stout prisms, m.p 266°–267° $[\alpha]_D^{10} - 95{\cdot}8°$ in alcohol, occurring in the bulbs of the wild daffodil *Narcissus pseudo narcissus* (Linn.) (Ewins, Chem. Soc. Trans. 1910, 97, 2406) and J. *Buphane disticha* (Herb.) (Tutin, *ibid.* 1911, 99, 1244) is a monacid tertiary base, sparingly soluble in the usual organic solvents. It contains no methoxyl groups, but on fusion with potash gives an amorphous polyphenolic derivative. Its physiological action is negligible.

Asahina and Sugi (Arch. Pharm. 1913, 251, 357) consider narcissine to be identical with lycorine (*q.v.*).

NARCOFORM, NARCYL, *v.* SYNTHETIC DRUGS.

NARCOPIN. Compound of narcotine and morphine meconate.

NARCOTINE *v.* OPIUM.

NARGOL. Silver nucleinate, used as a bactericide.

NARINGIN $C_{21}H_{26}O_{11}$. A glucoside obtained from the blossoms and fruit of *Citrus decumana* (Murr.). It is a white substance which dissolves in alcohol and in warm water, and crystallises with 4 mols. H_2O; sp. rotatory power in aqueous solution $[\alpha]_D = 84{\cdot}5°$; in alcoholic solution $[\alpha]_D = 87{\cdot}6°$. By hydrolysis is resolved into *isodulcit* (or a mixture of rhamnose and dextrose, Zoller) and *naringenin* $C_{15}H_{12}O_5$, a white crystalline substance, m.p. 248° with decomposition. Gives a deep-brown-coloured solution with ferric chloride, and is readily soluble in alcohol, ether, and benzene. Naringenin is readily decomposed when boiled with conc. KOH, into phloroglucinol and *naringenic acid* C_9H_8O, a white crystalline powder, m.p. 207°, soluble in water, giving a red-brown-coloured solution with ferric chloride. Its aqueous solution treated with sodium amalgam gives *hydronaringeninic acid* ($C_9H_{10}O_3$), m.p. 126° (W. Will, Ber. 20, 294) (*v.* GLUCOSIDES).

NARRAWOOD, *Pterocarpus spp.*, a well-known Philippine wood, according to Brooks (Philippine Journal of Science, 1910, v. 448), contains constituents very similar to those of sanderswood. To isolate the red colouring matter, the wood shavings were extracted with alcohol, the alcoholic extract concentrated and three volumes of water added. The solution was boiled to remove alcohol, and the red amorphous mass, which had then separated, was digested with about five parts of chloroform.

Thus obtained, *Narrin* consisted of a dark red amorphous powder, readily soluble in alcohol and insoluble in chloroform, which could not be obtained in a crystalline state. According to Brooks it is not identical with the santalin of sanderswood, for a preparation of this melted at 104°, whereas narrin does not melt but swells with charring about 180°. When fused with alkali narrin gives *phloroglucinol* and *resorcinol*, and by a slow oxidation with permanganate 12 grams gave 0·5 gram of a substance possessing a strong odour of *vanillin*. That it consisted of this substance was confirmed by its conversion into the phenylhydrazone which melted at 104°. By distillation with zinc-dust narrin yields a small amount of *resorcinol dimethyl ether*. Narrin, like santalin, gives with alcoholic potassium acetate a precipitate of potassium salt, and the copper salt prepared in this way with copper acetate had the composition $(C_{15}H_{13}O_6)_2Cu$.

The dyeing properties of narrin are similar to those of santalin, but the shades produced are not very fast to soap.

In addition to colouring matter, Brooks isolated from narrawood both *ptero-carpin* and *homoptero-carpin*. By a careful examination of these substances he concluded that the formulæ previously assigned to them are incorrect, and should in reality be, respectively, $C_{14}H_{12}O_4$ and $C_{17}H_{16}O_4$ (*see* Sanderswood). A. G. P.

NATRAJAROSITE *v.* Jarosite.

NATROLITE. One of the commonest of the several minerals belonging to the zeolite group of hydrated silicates. Its composition is $Na_2Al_2Si_3O_{10},2H_2O$, and it crystallises in the orthorhombic system, sometimes as square prisms, but more often as fine needles. It is usually found as radiating fibrous masses in the steam-cavities of volcanic rocks. Sp.gr. 2·25 Colour, usually white; lustre, vitreous. Compact, radially-fibrous material with concentric yellow bands, from Hohentwiel in Würtemberg, has occasionally been cut and polished for ornamental purposes. L. J. S.

NATRON. A mineralogical term (from the ancient νίτρον, soda) for the hydrated sodium carbonate $Na_2CO_3,10H_2O$, crystallising in the monoclinic system. Since this hydrate crystallises only at temperatures below 20°, it is only under exceptional conditions that it is likely to be found in the natron or soda lakes of desert regions; and if formed it would soon effloresce into the monohydrate Na_2CO_3,H_2O, known as thermonatrite. According to Dana it exists only in solution. The native soda met with in the regions of natron lakes consists for the most part of the salt $Na_2CO_3{\cdot}NaHCO_3,2H_2O$ known as trona, together with thenardite (Na_2SO_4) and halite (NaCl) (*v.* Trona). L. J. S.

NEAPOLITAN YELLOW *v.* Antimony.

NEAPON (*pantopon*). Trade name for a mixture of the soluble hydrochlorides of opium alkaloids.

NEAT'S FOOT OIL. Neat's foot oil (*Oleum bubulum* of the B.P.) is obtained from the feet of cattle by boiling with water. In this country the preparation of neat's foot oil is chiefly carried out in small establishments, in which the by-products and waste material of the slaughter-houses are worked up ('tripe shops'). The feet are carefully scraped and washed, the hoofs are cut off, and after the hair has been removed, they are boiled with water in jacketed pans heated by steam, the water being kept simmering for 8–10 hours. The oil rises to the top, and is skimmed off from time to time by means of suitable skimmers.

On a large scale, neat's foot oil is obtained as a by-product in the centres of the meat-packing trade (Chicago, South America). There the feet are taken in their fresh state from the slaughter-houses and sawn by a circular saw into suitable sizes for further treatment. The chief object of sawing off the feet is to separate the more costly shin bones from the feet proper, which latter yield the genuine neat's foot oil. The fatty matter contained in the shin bones approaches somewhat in consistence horse- or beef-marrow fat, as the case may be. When kept separate it is sold as 'bone oil.' This oil must not be confounded with neat's foot oil, nor with bone fat. It is, however, customary in America to recover the oil from the shin bones, together with the neat's foot oil, by boiling the shin bones with the feet. Therefore American oil has a higher solidifying-point than that prepared in this country. The feet are scalded by immersion in boiling water from 10 to 15 minutes in order to loosen the hoofs, which are removed.

The oil is skimmed off as it rises to the surface, filtered roughly through a fine wire screen, separated from water as far as possible, and then run into vessels provided with closed steam coils. Steam is passed through the coils and the water still contained in the oil thereby driven off, while at the same time organic impurities (albumin) become coagulated. The dried oil is finally obtained in a perfectly limpid state by filtering.

Neat's foot oil is pale yellow and has a bland taste. For the chemical and physical characters of the oil, *see* Oils, Fixed, and Fats, tables. Properly prepared oil contains only a very small amount of free fatty acids. On standing, the oil deposits 'stearine.' This 'stearine' is frequently removed by filtering at a low temperature; this is done especially in the preparation of neat's foot oil for the leather industries, in which oil of a low 'cold test' is required. Owing to its comparatively high price neat's foot oil is largely adulterated with vegetable oils, fish oils, and even mineral oils. For the detection of the adulterants, *see* Lewkowitsch, Chem. Techn.

Neat's foot oil is a valuable lubricating oil for clocks, guns, sewing machines, and other delicate machinery. It is largely used in the leather industries ('fat liquor'). J. L.

NEBULIUM (*archonium*). A gaseous element detected in the nebula of Orion by Bourget, Fabry and Buisson (Compt. rend. 1914, 158, 1017), which gives a strong double line in the ultra-violet 3726–3729, and which from interference measurements has an atomic weight of about 3. Possibly identical with the hydrogen isotope of J. J. Thomson, or with the helium isotope of Rutherford of mass 3.

NEEDLE-ORE or **AIKINITE** $PbCuBiS_3$.

NELSONITE *v.* Rutile.

NEMALITE *v.* Brucite.

NEODYMIUM. Sym. Nd. At.wt. 144·2 (Baxter), 144·4 (Garnier). The fractionation of the cerite earths by Mosander in 1842 led to the separation of a new oxide, to the supposed element of which the name '*Didymium*' was given, on account of the constant association of this substance with the metal lanthanum.

In 1879 the didymium earths yielded another element, samarium (Lecoq de Boisbaudran, Compt. rend. 88, 323), and six years later Auer von Welsbach succeeded in resolving 'didymium' into two components *neodymium* and *praseodymium* by the systematic fractional crystallisation of the double ammonium and sodium nitrates (Monatsh. 1885, 6, 477).

Occurrence.—In the minerals cerite, orthite, ytterbite, aeschynite, monazite, and samarskite.

According to Wherry (J. Washington Acad. Sci., 1917, 7, 143) the red-violet colour in certain minerals is due to neodymium, the absorption spectrum of which is observed in apatites from Ontario and California, and in reddish-violet calcites.

Separation. (I.) *Fractional precipitation methods* depending on differences in basic strength (*v.* LANTHANUM).

(II.) *Crystallisation methods.*—The rare earth nitrates in aqueous solution are acidified with one-tenth of their weight of nitric acid and treated with the calculated amount of ammonium nitrate, the liquid being then evaporated to the crystallising-point and left for 24 hours. The mother liquor is again concentrated to the crystallising-point and the process repeated 6–8 times. The fractions thus obtained are again systematically crystallised and the cycle of operations repeated many times until finally the lanthanum ammonium nitrate separates in the least soluble fractions, followed successively by the praseodymium and neodymium double salts. The course of the separation is to some extent indicated by the colour differences of the various fractions; those richest in lanthanum are colourless, then follow successively green fractions containing chiefly praseodymium and some colourless fractions in which the neutral tint is due to the complementary colours of praseodymium and neodymium salts. The more soluble fractions show the pink colour of neodymium salts, and finally the uncrystallisable mother liquors contain the very soluble salts of samarium and the terbium and yttrium metals. Owing to the presence of these soluble salts the neodymium fractions do not crystallise readily, and it is therefore convenient to remove the yttrium earths by a basic process and then convert the crude neodymium salt into double sodium nitrate. The crystallisation of this double salt furnishes fractions still containing praseodymium, and this component is the more readily separated from neodymium by the addition of lanthanum, with which it subsequently crystallises in the least soluble fractions.

Although the proportions of neodymium and praseodymium present in the rare earths vary within wide limits, yet 'didymium' solutions generally have a pink colour owing to the predominance of the former component.

Various modifications of von Welsbach's process have been introduced. After removing the main portion of the lanthanum the separation of praseodymium is accelerated by the addition of pure cerous ammonium nitrate, the cerous and praseodymium double salts crystallising together (Schéele, Ber. 1899, 32, 409; *cf.* Dennis and Chamot, J. Amer. Chem. Soc. 1897, 19, 799).

The manganous double nitrates, when crystallised from strong nitric acid give only a small amount of the middle fractions containing mixed praseodymium and neodymium salts, and bring about a sharp separation between the latter metal and samarium (Lacombe, Bull. Soc. chim. 1904, [iii.] 31, 570).

The magnesium double nitrates

$$2R(NO_3)_3,3Mg(NO_3)_2,24H_2O$$

have been employed in acid, neutral and slightly basic solutions. In this process a preliminary separation is sometimes effected by means of moderately concentrated potassium carbonate when lanthanum and praseodymium are concentrated in the precipitate whilst neodymium, samarium, and the yttrium metals accumulate in the filtrate (Demarçay, Compt. rend. 1900, 130, 1019, 1185; Drossbach, Ber. 1902, 35, 2826; Muthmann and Weiss, Annalen, 1904, 331, 1).

Fractionation of the oxalates has been used in freeing praseodymium from lanthanum, and neodymium from samarium (Schéele, *l.c.*; R. T. Meyer, Zeitsch. anorg. Chem. 1904, 41, 94).

Purification of neodymium and praseodymium. Neodymium is freed from samarium and the yttrium metals by continued crystallisation of the double nitrates and finally by fractional precipitation with ammonia.

The *m*-nitrobenzenesulphonates have been suggested as a means of obtaining pure neodymium preparations (Holmberg, Bihang. Sv. Vet. Akad. Handl. 1903, 28, II. No. 5; Chem. Centr. 1906, ii. 1595).

Fractional precipitation of neodymium chloride with hydrogen chloride serves to free neodymium from lanthanum (Baskerville and Stevenson, J. Amer. Chem. Soc. 1904, 26, 54).

Praseodymium sulphate is approximately twice as soluble in water as neodymium sulphate at temperatures ranging from 10° to 70°, and this difference has been utilised in separating the two elements (Muthmann and Rölig, Ber. 1898, 31, 1718).

Fractional crystallisation of the picrates affords a useful method for removing small quantities of the metals of the didymium group from those of the erbium and yttrium groups, and also for separating yttrium from erbium and holmium, but does not effect a separation of neodymium from praseodymium (Dennis and Rhodes, J. Amer. Chem. Soc. 1915, 37, 807).

It is scarcely possible to free praseodymium from last traces of lanthanum, but the following means have been recommended: crystallisation of oxalates (Feit and Przibylla, Zeitsch. anorg. Chem. 1905, 43, 202); crystallisation of citrates (Baskerville and Turrentine, J. Amer. Chem. Soc. 1904, 26, 46; Zeitsch. anorg. Chem. 1905, 45, 86; *cf.* R. J. Meyer, *ibid.* 1904, 41, 94); fusion of nitrates with potassium nitrate when praseodymium dioxide and basic lanthanum nitrate are produced, the latter being extracted with cold aqueous ammonium nitrate; oxidation with potassium permanganate and mercuric oxide followed by the gradual addition of cerous chloride when the higher oxides of praseodymium and cerium are precipitated, the lanthanum remaining in solution (Orloff, Chem. Zeit. 1907, 31, 115).

Neodymium is a paramagnetic metal of sp.gr. 6·956, m.p. 840°, obtained by electrolysing the fused chloride (Annalen, 1902, 320, 231; 1904, 331, 1), has a pale-yellow tinge; when heated at 220° in hydrogen it absorbs the gas forming the hydride NdH_2.

Neodymium carbide NdC_2, yellow hexagonal plates, sp.gr. 5·15, produced by heating the oxide with sugar carbon in the electric furnace (900 ampères, 50 volts); is decomposed by water evolving approximately 66 p.c. of acetylene, 6 p.c. of olefines, and 28 p.c. of paraffins (Moissan, Compt. rend. 1900, 131, 595).

Neodymium sulphide Nd_2S_3, olive green, sp.gr. 5·179, obtained by passing hydrogen sulphide over the heated sulphate or sulphur vapour over the carbide (Ber. 1899, 32, 3413).

Neodymium fluoride NdF_3, lilac crystalline powder, precipitated by hydrofluoric acid from a warm solution of the nitrate (Ber. 1908, 41, 634).

Neodymium chloride $NdCl_3$, a crystalline pink hygroscopic mass of sp.gr. 4·134 at 20°/4, prepared by (1) dehydrating the hydroxide in a current of hydrogen chloride; (2) heating the oxide or sulphate in chlorine and sulphur chloride (Matignon, Compt. rend. 1901, 133, 289; 1904, 138, 631); (3) decomposition of the sulphide with hydrogen chloride (Muthmann and Stützel, Ber. 1899, 32, 3413). The anhydrous salt absorbs from 2 to 12 molecular proportions of ammonia, and is slowly converted by dry air into the oxychloride NdOCl. The hexahydrate $NdCl_3,6H_2O$ separates from aqueous or aqueous-alcoholic solution in pink rhombic crystals (Ann. Chim. Phys. 1906, [vii.] 8, 243; Ber. 1902, 35, 2622).

Neodymium bromide and **iodide** are produced respectively by warming the anhydrous chloride in hydrogen bromide and iodide; the latter is a black crystalline mass (Compt. rend. 1905, 140, 1637).

Neodymium hydroxide $Nd(OH)_3$, obtained as a bluish-white precipitate from soluble neodymium salts by the action of caustic alkalis or ammonia (Zeitsch. anorg. Chem. 1905, 43, 267; Joye and Garnier, Compt. rend. 1912, 154, 510).

Neodymium oxide (*neodymia*) Nd_2O_3, a pale blue powder with violet tinge, prepared by heating the hydroxide, oxalate, nitrate, &c. The colour of the oxide depends partly on the mode of preparation, but also on the degree of hydration (Monatsh. 1885, 6, 477; Amer. Chem. J. 1898, 20, 345; Compt. rend. 1898, 126, 1039; Annalen, 1904, 331, 1; J. Amer. Chem. Soc. 1904, 26, 54; Bull. Soc. chim. 1904, [iii.] 31, 570; Garnier, Arch. Sci. phys. nat. 1915, [vi.] 40, 93 and 199). Higher oxides have been described: NdO_2 by Brauner (Zeitsch. anorg. Chem. 1902, 32, 1) and Nd_4O_7, by Waegner (*ibid.* 1904, 42, 118).

Neodymium nitrate $Nd(NO_3)_3,6H_2O$ (for isodimorphism with bismuth nitrate, *v.* Bodman, Ber. 1898, 31, 1237) furnishes the following double nitrates—

$$2Nd(NO_3)_3,3Mg(NO_3)_2,24H_2O$$
$$Nd(NO_3)_3,2NH_4NO_3,4H_2O$$
$$\text{and } Nd(NO_3)_3,2RbNO_3,4H_2O\ ,$$

(Zeitsch. anorg. Chem. 1911, 69, 221).

Neodymium chromate, moss green mass (Chem. Zeit. 1907, 31, 562).

Neodymium carbonate $Nd_2(CO_3)_3$, a pale red precipitate readily soluble in excess of alkali carbonates forming double carbonates

$$Nd_2(CO_3)_3,R_2CO_3$$

the solutions of which are blue and exhibit absorption spectra differing as to the position and intensity of the bands from those of simpler neodymium salts.

Neodymium cobalticyanide

$$Nd_2(CoC_6N_6)_2,9H_2O$$

1000 parts of a 10 p.c. HCl solution contain 4·19 parts of the salt.

Neodymium oxalate $Nd_2(C_2O_4)_3,10H_2O$ with the exception of thorium oxalate is the least soluble in acids of any of the rare earth oxalates.

Neodymium acetylacetonate

$$Nd[CH(CO{\cdot}CH_3)_2]_3$$

violet crystalline mass, m.p 144°–146°, its molecular weight in ethyl sulphide is double that indicated by the foregoing formula.

Neodymium dimethyl phosphate

$$Nd_2(Me_2PO_4)_6$$

lilac-coloured, hexagonal plates, solubility 56·1 at 25° and 22·3 at 95°.

For other salts *v.* James, Hoben and Robinson (J. Amer. Chem. Soc. 1912, 34, 276; Morgan and James, *ibid.* 1914, 36, 10).

The *absorption spectrum* of neodymium is much more complex than that of praseodymium. A 10 p.c. neodymium chloride solution shows upwards of 17 bands, and 29 (range λ742–λ328) have been noticed on dilution (Le Radium, 1909, 6, 215; Compt. rend. 1898, 126, 1039; Proc. Amer. Phil. Soc. 1908, 47, 276; Jones and Guy, Physikal. Zeitsch. 1912, 13, 649).

For *spark* and *arc spectra* *v.* Exner and Haschek, Sitzungsber. Wien. 1899, II*a*. 108, 1088; Die Wellenlangen der Bogenspektra, 1904; Zeit. wiss. Photograph. Photophys. Photochem. 1906, 3, 411, 4, 16.

Thermochemistry of neodymium compounds (*v.* Matignon, Compt. rend. 1905, 141, 53).

Physiological action of neodymium salts (*v.* Amer. J. Physiol. 1906, 16, 314; Proc. Phys. Soc. 1910, 68).

G. T. M.

NEOFORM. Trade name for a bismuth compound of tri-iodophenol.

NEOGEN. An alloy resembling silver in colour, said to have the following composition (Sauvage, Dingl. poly. J. 215, 377):

Cu	Zn	Ni	Sn	Al	Bi
58·0	27·0	12·0	2·0	0·5	0·5

NEOHEXAL. Sulphosalicylic compound of hexamethylenetetramine.

NEOLEPTOL. Syn. for Triformyltrimethylenetriamine.

NEON. Sym. Ne. At.wt. 20·2 (Watson; 20·15, Leduc). An inert gas, discovered by Ramsay and Travers in the lighter portions of gas obtained by fractionating 15 litres of crude argon (Proc. Roy. Soc. 1898, 63, 438; Phil. Trans. 1901, 47). The method employed in the separation of neon from the accompanying helium and argon is fully described in Travers' Study of Gases, 212-218. To obtain a gas rich in neon (and helium), the gas escaping from an air liquefier is used. This gas is chiefly nitrogen; it is liquefied and a current of air blown through the liquid. The first portion of the liquid to evaporate contains nearly all the neon and helium present. After removing oxygen and nitrogen, the argon is separated by fractional evaporation at the temperature of liquid air. To separate neon from helium effectively, fractionation must be carried out at the temperature of liquid hydrogen (*cf.* Watson, Chem. Soc. Trans. 1910, 97, 810). Neon and helium may be separated from the remaining inert gases by absorbing the latter in charcoal at the temperature of liquid air (Valentiner and Schmidt, Sitzungber. K. Akad. Wiss. Berlin, 1905, 38, 816). They may also be separated by cooling in liquid hydrogen when neon solidifies, the helium (b.p. −269°) remaining as a gas.

According to Ramsay, neon is either a product of degradation of niton, or, more probably, produced by the action of niton on water.

Neon is much more abundant in the atmosphere than krypton and xenon; 1 million volumes of air contain 15 volumes of neon (Claude, Compt. rend. 1909, 148, 1454; *cf.* Watson, Chem. Soc. Trans. 1910, 97, 810; Ramsay, Proc. Roy. Soc. 1905, 76, A, 111; 1908, 80, A, 599). It also occurs in the gases evolved from many thermal springs (Moureu and Biquard, Compt. rend. 1906, 143, 180; Ramsay, Chem. Soc. Trans. 1912, 101, 1367).

Neon is a colourless, odourless, tasteless gas of sp.gr. 0·695 (air=1) (Leduc, Compt. rend. 1914, 158, 864). Next to helium and hydrogen, it is the least easily condensible gas known. Its critical temperature is below −218°; at the temperature of liquid hydrogen it solidifies. The critical pressure is 29 atmospheres, and the triple-point pressure for the system solid-liquid-gas is 35 cm. (Onnes, Proc. K. Akad. Wetensch. Amsterdam, 1909, 12, 175). The vapour pressures of liquid neon between 24·42° and 44·43° (abs.) may be reproduced by the formula $T \log p = -65{\cdot}061 + 2{\cdot}8191T + 0{\cdot}011181T^2$, where p=vapour pressure in atmospheres (Cath and Kamerlingh Onnes). At N.T.P. 1 litre of neon weighs 0·9002±0·0003 grams (Watson, Chem. Soc. Trans. 1910, 97, 832). The compressibility of the gas has been studied by Burt (Trans. Faraday Soc. 1910, 6, 19). The refractive index of neon at N.T.P. for the green mercury line (λ−5461) is 1·0000672 (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1910, 83, A, 149). The coefficient of departure from Boyle's law is -6×10^{-6} per cm. of mercury at 17° between 1 and 5 atmos.; hence the molecular volume at 10° and 760 mm. Hg is 1·0004 (perfect gas=1, hydrogen 1·0006). coefficient of dilatation, $\beta = 3664 \times 10_{-}{}^{6}$; density, 0·695; atomic weight, 20·15 (Leduc); for its viscosity, *v.* Rankine (Proc. Roy. Soc. 1910, 83, A, 516). Neon is slightly soluble in water, the absorption coefficient at 20° being 0·0147, and 0·0322 at 50° (Antropoff, *ibid.* 1910, 83, A, 474).

When neon is shaken in a tube with mercury, a red glow is observed, which is as bright at 120–200 mm. as at 760 mm. On long shaking, the glow ceases to appear; but the property is restored by sparking the gas. Moisture must be absent; hydrogen does not seriously affect the glow, which is more pronounced in a silica tube than in one of glass (Collie, Proc. Roy. Soc. 1909, 82, A, 378). For the spectrum of neon, *v.* Baly (*ibid.* 1903, 72, 84; Phil. Trans. 1903, A, 202, 183); Liveing and Dewar (Proc. Roy. Soc. 1901, 68, 389); Purvis (Proc. Camb. Phil. Soc. 1909, 15, 45); Watson (Proc. Camb. Phil. Soc. 1911, 16, 130); Merton (Proc. Roy. Soc. 1914, A, 89, 447); Meissmer (Ann. Physik, 1919, [iv.] 58, 333); Paschen (*ibid.* 60, 405).

Neon is monatomic, since the ratio of its specific heat is 1·66 (Ramsay and Travers).

According to Aston (Phil. Mag. 1920, 39, 449) neon is a mixture of at least two isotopes having the atomic weights 20·00 and 22·00 respectively, 90 p.c. of the former to 10 p.c. of the latter. It is possible that an isotope of mass 21 is present to the extent of less than 1 p.c.

NEOPINE. Syn. for Hydroxycodeine, *v.* Opium.

NEOPYRIN. Syn. for Valerylamino antipyrine.

NEOSALVARSAN, NEOARSENPHENAMINE, NEODIARSINAL. Sodium 3·3′-diamino-4-4′ dihydroxyarsenobenzene-N-methylene-sulphinate. *See* Arsenicals, organic.

NEOSIODE. Syn. for Iodocatechin.

NEOYTTERBIUM. *See* Ytterbium.

NEPHELITE or **NEPHELINE.** A rock-forming mineral consisting of sodium (and potassium) alumino-silicate crystallised in the hexagonal system. In composition it approximates to the orthosilicate formula $NaAlSiO_4$, but there is always a slight excess of silica. This has been explained by the presence of such molecules as $KAlSi_2O_6$ (leucite) and $NaAlSi_3O_8$ (albite), or by the solid solution of silica in the material. Potassium (K_2O 4–7 p.c.) replaces sodium in the ratio of 1 : 3 or 1 : 5. Calcium (CaO 1–2 p.c.) is also often present. Other members of this hexagonal group of minerals, namely, *kaliophilite* ($KAlSiO_4$) and *eucryptite* ($LiAlSiO_4$), do not show the same variations in composition. These, as well as the normal sodium orthosilicate ($NaAlSiO_4$) and the corresponding barium and strontium compounds, have been prepared artificially. The mineral is readily decomposed by acids with gelatinisation; and it is completely soluble in dilute (N/4) hydrochloric acid. Sp.gr. 2·55–2·65; H. 5½–6. Two varieties are distinguished, namely, 'glassy' nephelite and 'greasy' nephelite or *elaeolite* (Ger. Fettstein). The former occurs as small colourless crystals and grains in volcanic rocks rich in soda, such as phonolites and nepheline-basalts. The best crystals are from Vesuvius. Elaeolite occurs as larger opaque masses, of a grey, bluish, greenish, or red colour, in plutonic rocks (nepheline-syenite). Its characteristic greasy lustre is due to numerous microscopic enclosures of other minerals. This variety is occasionally employed as a gem-stone. When cut with a curved surface it displays a chatoyant effect like cat's-eye. This is the only practical use to which the mineral is put. But, being readily decomposed by acids and in certain places (south Norway, southern Urals, Ontario, Brazil, &c.) of abundant occurrence, it might be employed as a source of potash. This would particularly apply to the closely allied mineral kaliophilite (K_2O 29·7 p.c.), were it not of such rare occurrence, being known only in very small quantity from Vesuvius. It must be remembered that nepheline-syenite is of some importance as the home of many rare-earth minerals. L. J. S.

NEPHELOMETRY. In the course of investigations liquids are sometimes obtained holding in suspension extremely small quantities of solids, and having in consequence an opalescent appearance. Such suspended matter cannot conveniently be separated and weighed. Richards, in a paper on a revision of the atomic weight of strontium involving the formation of silver bromide (Proc. Amer. Acad. Arts and Sciences, 1894–1895, 30, 384; and Zeitsch. anorg. Chem. 1895, 8, 268), described an instrument which he had devised for comparing opalescences and estimating their relative amounts. He named it a *nephelometer*, from *νεφέλη, a cloud*; it was designed to compare the light reflected by two opalescent liquids, one being the liquid under examination and the other a liquid containing an opalescence caused by a known quantity of material. By varying the lengths of two columns of liquid exposed to light an equality of brightness, as viewed from above, was attained, and then the lengths of the columns were measured. In the instrument pure water, even when exposed to a strong light, seemed absolutely black; but an absurdly small quantity of precipitate, which no ordinary means could discover, made a very evident cloudiness.

Early attempts at comparing opalescences were made by Mulder (Die Silberprobiermethode, Trans. by Grimm, 1859), and by Stas (Ann. Chim. Phys. 1874, [5], 3, 145); his method was one of turbidimetry.

Nephelometry ought to be distinguished from turbidimetry. In the latter light is viewed *through* the opalescent liquid and the power of cutting off some of the light is the basis of comparison, whilst in nephelometry the intensity of the light reflected by the particles in suspension is the basis; *i.e.* the light from what is sometimes called the Tyndall beam. Unfortunately, authors have mixed up the use of these terms and of *nephelometer* and *turbidimeter*, and their writings must be read carefully to find out which they really mean.

Opalescences too slight to be measured by turbidimetry can be measured by nephelometry.

Nephelometry has become a valuable aid to research. It has been used in some other redeterminations of atomic weights, for example, those of sodium and chlorine (Richards and Wells, J. Amer. Chem. Soc. 1905, 27, 484); strontium (Richards, Zeitsch. anorg. Chem. 1905, 47, 145); potassium (Richards and Staehler, Ber. 1906, 39, 3621); and vanadium (Briscoe and Little, Chem. Soc. Trans. 1914, 105, 1310). More recently it has been adapted for various investigations in biological chemistry where the quantities of material available are small and the amounts to be determined are far smaller. It has also been proposed to make various analytical estimations by producing opalescences and measuring them with the nephelometer.

Nephelometers.—*Richards' Nephelometer.*—Richards and Wells, in Amer. Chem. J. 1904, 31, 235, describe an improved form of the earlier instrument. This improved form is shown in Fig. 1. By its means the amount of precipitate can be estimated when less than one or two milligrams per litre are in suspension. The liquids to be compared are contained in the two test tubes, *t*, *t*, each of a capacity of 32 c.c. and of the same diameter, made of clear glass free from striations.

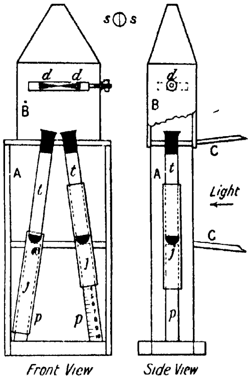


FIG. 1.

In order to avoid reflections from the liquid meniscus at the top and from the curved surface of the glass at the bottom, they are painted outside round the top and bottom with black asphalt paint, the distance between the bands of paint being exactly the same in each tube. These tubes are held in a frame A, where they rest on pillars, *p*, *p*, slightly inclined towards each other. Glass jackets, *j*, *j*, also painted to make them opaque, slide up and down over the tubes and pillars, and can be kept in any desired position by brass springs, thus excluding the light from more or less of the liquids in the tubes, and in consequence only that portion of the opalescence exposed sends light up to the prisms *d*, *d*. The source of light is an incandescent electric lamp contained in the large box, CC. Scales on the pillars show how much of the clear portion of each tube is exposed. On the top of the frame is a movable box, B, blackened inside, and carrying two prisms, *d*, *d*, with angles of 15°, with their thin edges slightly ground and fitting closely together. By means of these prisms an observer looking down through the aperture at the top of the box sees semicircular images, *s*, *s*, of about half the cross section of each tube with a common diameter, as in the ordinary half-shade polarimeter, the two halves appearing scarcely larger than a single tube; thus their relative brightness can be readily compared. By adjusting the jackets at various heights the two half circles can be made of equal brightness and the lengths of the tubes exposed can be read off on the scales. The liquids are stirred and mixed by means of propeller-shaped pieces of platinum foil sealed on two glass rods; these are kept standing in separate tubes of pure water when not in use. In the earlier instrument there were no prisms, so the brightness of the opalescences could not be so accurately compared.

Roughly speaking, the amounts of substance in suspension are inversely proportional to the lengths exposed when equal brightness is attained. Thus, if the prepared liquid contains 0·025 milligram of precipitate and the scales show that an exposure of 9·0 centimetres gives the same brightness as 10·0 centimetres of the liquid under examination, then the latter is the weaker and contains nine-tenths of 0·025 that is 0·0225 milligram of precipitate. This rule, however, is not strictly correct, for the upper particles must hide to some extent those lower down, and the method is quite inapplicable if the precipitate is at all abundant; but for slight opalescences the error is not great, especially when the lengths exposed differ but little. To ensure accuracy a series of observations should be made and the mean taken. A rough experiment should first be made with liquids approximately equal in length for the same brightness and then observations with liquids made very nearly equal by calculation from the first experiment.

Many precautions must be taken to ensure accuracy; thus stray reflections in the apparatus must be avoided, as also must minute air bubbles produced in mixing the liquids, and dust must be guarded against—it is often present in distilled water, and would cause an opalescence. When silver solutions are dealt with dust would also increase the precipitate, as it usually contains chlorides. The traces of hydrochloric acid commonly present in laboratory air and which get into the distilled water would also precipitate the silver, as also would the chlorides of the perspiration if the glass surfaces are touched or handled. To prevent darkening silver precipitates must be prepared in a dim light in a dark room, and must be kept in perfect darkness except for the short exposure to light necessary when making an observation.

The most important precaution of all is to ensure that the standard opalescence and the one to be estimated are strictly comparable, and this is not at all easy to attain. Opalescences vary according to the method of precipitation, the concentration of the solutions, the amount and nature of the other substances in solution, the amount and manner of stirring, and change in character as time goes on after their first formation. The rate of change, too, is different in different cases. The stirring should be done at the commencement of the precipitation, as delay alters the result. The property of changing with time will cause error if, when the comparison is made, the opalescence in one liquid is not so fully developed as that in the other, as may happen if the standard opalescence is produced a little differently from the one to be estimated.

The opalescence in the case of silver chloride, and, no doubt, in other cases, increases to a maximum and then diminishes. The course of the process seems to be that on adding the precipitant to the solution the silver chloride is first formed in particles too small to reflect light; as time goes on these aggregate in masses large enough to reflect light and to appear as an opalescence, and a maximum brightness is reached after which, by further aggregation, the masses become lumpy or flocculent, thus including particles shut off from the light, and the brightness lessens. As time goes on, too, some precipitate falls to the bottom, and thus diminishes the brightness.

In the case of silver chloride the opalescence varies a great deal according to circumstances, and much study has been given to it by Richards and by Wells (Amer. Chem. J. 1906, 35, 99 and 508). No doubt, other opalescences exhibit the same or other peculiarities, which must be ascertained if their measurement is to be accurate. Weak opalescences change much more slowly than strong ones, and consequently are more suitable for nephelometric measurement. Very slowly forming opalescences, in general, never attain the maxima that quickly forming ones attain. The presence of various substances in solution influences the maximum reached, and the time taken to reach it; it was found that electrolytes, such as nitric acid, usually increased the amount of the maximum and accelerated its arrival; results are given and anomalies are discussed in the paper. Consequently, a suitable time must be allowed for the opalescences to form, and this must be found by trial experiments. For every concentration suitable additional substances in solution and a suitable excess of the precipitant are required. For instance, Wells (Amer. Chem. J. 1906, 35, 113 and 509) recommends for silver nitrate added to potassium chloride N × 0·000005, that an electrolyte should be present, that the silver nitrate should be in one hundred-fold excess, and that the measurement should be made in 30 minutes, or more when the opalescence has become relatively stable. As the standard opalescence undergoes variation as well as the opalescence under examination, he substituted plates of ground glass in the nephelometer for the former, so as to have an invariable standard when watching the variations in brightness of the latter. Richards (*ibid.* 510) comments on Wells' work, and does not recommend this plan when nephelometry is used for analytical work. He insists that for even moderately accurate analytical results the unknown solutions to be estimated and the known standard solutions must have been precipitated and treated in exactly the same way, including temperature conditions, and sufficient time must have been allowed for the opalescences to develop. He considers that most of the opalescences examined by Wells were too strong for accurate nephelometric work, because of their rapid rate of change; and says that the nephelometer should be employed for exact work only when the precipitate is so finely divided that it will not in any reasonable time, for example, two or three days, deposit itself and thus place itself within the range of ordinary quantitative determination. He mentions not much over 1·5 milligrams of silver chloride per litre, or about N × 0·00001, as being a suitable strength.

As regards similarity of treatment: when ascertaining the amount of dissolved silver chloride in washings, by precipitation with silver nitrate, he did not consider it satisfactory to compare the opalescence with a standard made by adding silver nitrate to a known weight of potassium chloride, but first dissolved both opalescences in ammonia and reprecipitated them with nitric acid before using the nephelometer (Ber. 1906, 39, 3622). The reason why he took this precaution was that he had noticed that when adding a large excess of silver nitrate to solution of silver chloride the opalescence formed more quickly than when adding it to an equivalent solution of sodium chloride. This led him to doubt whether the weights of precipitate corresponding to a given maximum intensity of opalescence are equal in the two cases. Another peculiarity that he noticed was, that if a solution of silver chloride was long kept, it lost in strength without any deposit being visible on the glass. One such solution fell from about 1·5 milligrams per litre to 1·1 milligrams. This points to the need of not delaying the precipitation and nephelometric measurement of such weak solutions (J. Amer. Chem. Soc. 1905, 27, 486).

Lamb, Carleton and Meldrum (J. Amer. Chem Soc. 1920, 42, 251) give a study of silver chloride opalescence in a 50 p.c. alcohol and water mixture, after heating to 40°, for war-gas work; use of kieselguhr as a standard; additional precautions to those of Richards and Wells, *e.g.* the position of the eyepiece and tubes should be the same throughout a set of comparisons.

Kober's Nephelometer.—Kober has employed the method to study the action of enzymes on proteins (J Biol. Chem. 1912–13, 13, 485; and J. Amer. Chem Soc. 1913, 35, 290), and has devised a nephelometer (J. Ind. Eng. Chem. 1915, 7, 843) in which the lengths of the columns of liquid exposed to light are arrived at in a different way. It is somewhat on the plan of Duboscq's colorimeter, and is shown in side view in Fig. 2. It is one of several forms that he tried. The opalescent liquids are contained in two tubes like *t*. For clearness only one is shown, the other being mostly hidden. They are of clear glass except the bottoms, which are black and opaque. They rest on two shelves like *s*, which can be moved up and down by two rack-and-pinion arrangements like *r* at the back of the instrument, so as to reach the two fixed plungers, *p*, *p*. These are empty cylinders made of black glass with optically perfect plates of clear glass fused on to them at the bottom, thus avoiding the troubles arising from plungers painted black and closed by plates cemented on. By raising a shelf the plunger can be more or less deeply immersed in the liquid, and the column of liquid between the bottom of the plunger and the bottom of the tube is then exposed to the light coming from the case C, and the opalescence in this column then sends its light up through the plunger to the optical arrangement above. Scales at the back of the instrument show what lengths of liquid are exposed—these lengths may reach 100 millimetres. The optical arrangement is a set of prisms contained in the prism house *h*; it is based on the Lummer-Brodhun plan (Zeitsch. f Instrumentenkunde, 1889, 9, 23 and 41), and has the effect that as seen through the terrestrial eye-piece E, the light from one tube illuminates a square *q*, and the light from the other tube illuminates the rest of the circle *l*. By moving the shelves and thus altering the lengths of liquid exposed to light, *l* and *q* can be made of equal brightness. The openings, *a b c d*, on each side are closed by doors, and there are black curtains behind the tubes to give a black background. The inside of the apparatus is painted black to prevent reflections, and a board can be put between the two tubes for the same purpose. The part C is a wide cylinder containing an electric lamp. The filament should be compact so as to make the source of light as nearly a point as possible, and the lenses should project the light in a pencil of parallel or nearly parallel rays. This part, C, is not essential, some forms of the instrument are without it, and can be used with daylight. The hinge, H, allows the instrument to be inclined at any convenient angle. If mirrors are fixed at *m* and *m′* the instrument can be used as a colorimeter, but then the tubes must be replaced by others with clear glass bottoms. If the instrument is used in a photographic dark room, or if the eyepiece is surrounded by a box into which the observer can put his head, trouble from stray light at the eyepiece is avoided. Trials should be made to see if pure water in the tubes throws up any light to the eyepiece, and tubes with opalescences should be interchanged to see that the results are the same, using either side of the apparatus, and any necessary corrections must be ascertained.

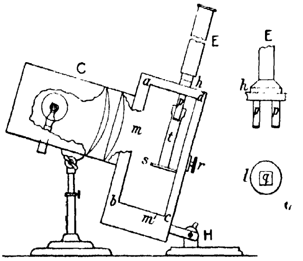


Fig. 2.

In J. Biol. Chem. 1917, 29, 155, Kober describes improvements in the mechanical, optical and lighting details of the instrument, and in J. Ind. Eng Chem. 1918, 10, 556, he gives numerous figures. Kober and Klett, in J Biol. Chem. 1921, 47, 19, give further improvements designed to make it more convenient to use and to avoid the fatigue that the earlier form caused when in constant use. As thus improved the instrument is made by the Klett Manufacturing Company, 202, East 46th Street, New York.

Kober's formula.—Whilst Richards thinks that the column of liquid examined and the column of the standard liquid should differ very little in length when equality of brightness is attained, if the results are to be accurate, Kober (J. Biol. Chem. 1912–13, 13, 491) proposes a formula, or a curve drawn on paper, by the use of which liquids of strengths ranging down to about half that of the standard can have their strength determined. He finds, as might be expected, that the simple inverse proportion rule does not hold good for this range, and gives this formula—

$$y = \frac{s}{x} - \frac{s(1-x)k}{x^2}$$

for finding x, which denotes the ratio of the unknown strength to the strength of the standard. In the formula s is the length of standard liquid exposed, y is the length of the liquid under examination when equality of brightness is attained, and k is a constant which has to be determined for the particular substance dealt with, and for the particular instrument. To test his formula he made experiments with the protein edestin, preparing the opalescences by precipitating a solution of it in hydrochloric acid by the addition of sodium chloride solution. He employed strengths ranging from 33·3 to 14·3 milligrams per litre, and from 16·6 to 5 milligrams per litre. He also experimented with silver chloride, using strengths ranging from 57 2 to 14·32, and from 14·32 to 7·16 milligrams per litre. He tested it again later (*ibid.* 1917. 29, 164), using casein precipitated by sulphosalicylic acid, and found that with his later instrument the value of *k* was different from that found in earlier experiments, showing that this constant varies with the instrument used as well as with the substance.

Bloor (J. Biol. Chem. 1915, 22, 145) describes a method of converting at will a Duboscq's colorimeter into a nephelometer by the use of certain accessories. In it the plungers are removed, and Richards' plan of using jackets to cut off the light is employed.

Marshall and Banks (Proc. Amer. Philos. Soc. 1915, 54, 176) have designed a form in which the upward light from *equal* columns of two opalescent liquids is compared and measured. The method is shown in side view in Fig 3, but without details. The columns are contained in the tubes *t*, *t′*. The light from *t* is reflected horizontally by the mirror *m*, which is silvered with the exception of a wide ring left transparent. The light from the other column in *t′* is also reflected horizontally by the mirror *m′*, so that it passes through the unsilvered ring on *m*. On viewing *m* through the magnifying eyepiece, E, the two lights are seen contrasted as shown at C. A wedge of neutral-tinted glass is then slid over *t* until the two lights are of equal brightness, and from the requisite thickness of this the relative brightness of the opalescences is calculated.

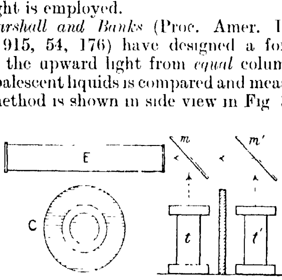


Fig. 3.

Briscoe and Little, when redetermining the atomic weight of vanadium (Chem. Soc. Trans. 1914, 105, 1321), used a nephelometer resembling Richards', but having the test-tubes vertical instead of inclined, and having two mirrors instead of the prisms. The near mirror reflects half the top area of the near test-tube, and the back mirror reflects the top area of the back test-tube, so that the two brightnesses are viewed from the side of the apparatus instead of from the top, and appear as semicircles side by side, like *s*, *s* in Fig. 1.

The Tyndallmeter of Mecklenburg and Valentiner (Zeitsch. für Instrumentenkunde, 1914, 34, 209) is an elaborate instrument, so named by them because it examines the light sent up by a beam such as Tyndall produced in floating dust (Nature, 1869–70, 1. 499). The following is a brief outline of the instrument. A beam of light from a Nernst lamp is divided; one part is made to proceed horizontally through the liquid under examination, where it produces a Tyndall beam with any suspended matter. Light that ascends vertically from this beam is viewed through an eyepiece, where it is seen contrasted with the light from the other part of the beam. This latter light has passed through three Nicol's prisms: two fixed and one rotatable. By rotating this through an angle which is measured, the brightness of this light can be reduced until it is equal to that from the suspended matter. Mecklenburg also writes about the Tyndallmeter (with figures) and the use of the Tyndall beam for colloid solutions in Kolloid Zeitsch. 1914, 14, 172; 1914, 15, 149; and 1915, 16, 97.

Tolman and Vliet (J. Amer. Chem. Soc. 1919, 41, 297) describe a somewhat similar Tyndallmeter for liquids, smokes, and mists; it was made in war time from pipe fittings and stock apparatus. Further papers in the same volume deal with results obtained in the case of silica suspensions in water and smokes.

Wilke and Handorsky (Ann. d. Physik, 1913, [4] 42, 1145) a Tyndallmeter not yet so named.

Dreyer and Gardner (Bio-Chem. J., 1916, 10, 399) prepare a set of graduated dilutions in small test-tubes and compare bacterial emulsions or liquids with matter in suspension with these.

Kleinmann's Nephelometer (Biochem. Zeitsch. 1919, 99, 129, and Kolloid Zeitsch. 1920, 27, 236) is an important rival of Kober's. It is somewhat like Kober's, but the amount of illuminated liquid under observation is regulated by admitting light through rectangular apertures, which can be increased or diminished by lowering or raising movable shutters, instead of being regulated by lowering or raising the vessels. The plungers are cylinders of solid glass instead of being hollow tubes, and the source of light is further off. It is made by Schmidt and Haensch, 16, Prinzessinnenstrasse, Berlin, S 42.

In the same volume of the Biochem. Zeitsch. Kleinmann writes at length on nephelometry, and criticises Kober's nephelometer and formula.

Weinberg (Biochem. Zeitsch. 1921, 125, 292) makes a critical comparison of Kober's and Kleinmann's instruments, and describes an improved form and also a form with a constant standard of comparison; in this two Nichol's prisms are used. He also gives details of procedure, criticises other authors' work, and thinks Kober's tubes are not wide enough.

Applications.—The following are some further references to nephelometric methods that have been proposed or used for the determination of various substances: (Kober, J. Soc. Chem. Ind. 1918, 37, 75T), A survey of these determinations, giving also a method for estimating the phosphorus in cast iron, and mentioning the use of solutions of colloids such as egg albumin, soluble starch, and gelatin, to keep opalescences in suspension. (Kober, J. Amer. Chem. Soc. 1913, 35, 290), Digestion of casein, using sulphosalicylic acid as a precipitant. (Kober, *ibid.* 1585), Determination of casein, globulin, and albumin in milk. (Marriott, J. Biol. Chem. 1913-14, 16, 289), Determination of minute quantities of acetone by means of a silver-mercury-cyanide reagent. (Bloor, *ibid.* 1914, 17, 377, and 1915, 23, 317), Determination of fat in small amounts of blood. By suitable treatment a solution of sodium salts of the fatty acids is obtained and then hydrochloric acid is added as a precipitant. (Sharpe, Biochem. J. 1917, 11, 96), Estimation of fatty acids and soaps in faeces. (Csonka, J. Biol. Chem. 1918, 34, 577, and 1920, 41, 243), Definition of 'nephelometric value;' Study of these values for cholesterol and fatty acids; Criticism of Bloor's work on fat in blood and of Sharpe's work on fatty acids in faeces. (Kober and Graves, J. Amer. Chem. Soc. *1914, 36, 1304*), Estimation of undigested nucleic acids by addition of egg albumin and acetic acid. (Graves, *ibid.* 1915, 37, 1171), Determination of ammonia by precipitation with a mercuric chloride-sodium chloride-lithium carbonate reagent, the precipitate being kept in suspension by starch solution. Kjeldahl-nitrogen determinations can be made without the need of distilling, but mercuric oxide should be used as the catalyst instead of copper sulphate. (Kober and Egerer, *ibid.* 2373), Estimation of phosphorus by means of a strychnine-molybdic acid reagent. (Kober and Graves, J. Chem. Soc. Absts. 1915, 108, [ii.] 602), Estimation of purine bases and uric acid in blood and urine. (Bloor, J. Biol. Chem. 1915, 22, 133, and 1916, 24, 447), Determination of lecithin in small amounts of blood by oxidising it to phosphoric acid and precipitating this with silver nitrate or with a strychnine-molybdic acid reagent. (Woodman, Gookin and Heath, J. Ind. Eng. Chem. 1916, 8, 128), Determination of small amounts of essential oils by precipitating their alcoholic solutions with water. (Lyman, J. Biol. Chem. 1917, 29, 169), Determination of calcium in blood and milk by coagulating with trichloracetic acid, filtering, and after suitable treatment of the filtrate, precipitating the calcium with a mixture of ammonium stearate and oleate. (Bloor, *ibid.* 1918, 36, 33), Determination in small amounts of blood of phosphoric acid, both total and in different blood components. (Meigs, *ibid.* p. 335), Determination of phosphorus. (Kleinmann, Biochem. Zeitsch. 1919, 99, 115 to 189), Estimation by the strychnine-molybdenum reagent of P_2O_5 in amounts from 0·1 milligram to 0·0005 milligram. (Yablick, Perrott and Furman, J Amer. Chem. Soc. 1920, 42, 266), Determination of mustard gas in war-gas work by the use of selenious acid. (Desha, *ibid.* p. 1350) uses ultra-violet rays to produce fluorescence in liquids placed in a Kober nephelometer.

Turbidimeters.—The simple plan of viewing a candle flame through a column of liquid, for rapid analyses and for water examination, is described by Hinds (J. Amer. Chem. Soc. 1896, 18, 661), by Jackson (*ibid.* 1901, 23, 799), by Muer (J. Ind. Eng. Chem. 1911, 3, 553), and in the U.S. Geological Survey Water Supply Paper No. 151, 1905. In this last there is also described a modification using an electric light and also a plan of using a platinum wire projecting from a rod to be viewed through the water; this is further dealt with by Wells in U.S Bureau of Standards Sci. Paper No. 367, 1920, where he describes another turbidimeter. Smith's apparatus (U.S. Pat. No. 1,232,989, 1917, and J. Soc. Chem. Ind. 1917, 36, 1031) is another electric light form of the candle plan.

Schlesinger (D. R. P. 237,470, 1910, and J. Soc. Chem. Ind. 1911, 30, 1413) describes a form in which light passes through a hole in a screen, then through a transparent grating, then through a wedge-shaped vessel containing the turbid liquid. The grating is viewed through the liquid and through a hole in another screen.

Lambert, Vlés and de Watteville (Compt. rend. 1919, 168, 797) describe a form for bacterial suspensions using for comparison a photographic plate of progressive darkening.

Sheppard (J. Ind. Eng. Chem. 1920, 12, 167) describes a form suitable for varnishes, solutions of gelatin and the like. In this use is made of the *bands* seen when the *lines* of two line gratings cross one another as described by Ives in the Electrical World, 1910, 55, 939, and in J. Opt. Soc. Amer. 1917, p. 100. The line gratings are situated at one end of the instrument, and light from a lamp passes through them. They can be rotated with respect to each other and the angle between the *lines* read off. A standard liquid is placed in a cell between the gratings and the eyepiece. The *lines* are now indistinguishable, and only *bands* are seen. The gratings are now rotated until the bands just disappear and only a uniform grey is seen, and the angle is read off. The same is done with the liquid under examination instead of the standard liquid, and the new angle is noted. From these two angles the relative transparency of the liquids is calculated. The liquids are contained in square glass jars, and to obviate distortions caused by their irregular sides, the jars are immersed in the cell in monochloronaphthalene the refractive index of which is the same as that of glass.

Bowers and Moyer (J. Biol. Chem. 1920, 42, 191) have designed a turbidimeter in which the plan of the oil spot photometer is used. The light from an electric lamp on one side passes through the liquid under examination; and the light from an electric lamp on the other side passes through two glass discs. There are two flat wheels in which ground glass discs are mounted, and these wheels are revolved until two glass discs are found which reduce the light until it is equal to that coming through the liquid. Some details seem to need fuller explanation in the paper.

Chénaveau and Audubert (Compt. rend. 1920, 170, 728) describe a turbidimeter (they call it a nephelometer) in which the light from an incandescent lamp is reflected by two totally reflecting prisms; the beam from one of them passes through a tube containing the liquid under examination, and the beam from the other passes through a plate designed to diminish the light in a measurable degree. This plate is made up of two similar prisms of very small angle; one is of glass of a neutral tint and the other is of clear glass, and they are cemented together in reversed positions so that the deviation of the beam caused by one prism is corrected by the other. By sliding this plate different thicknesses of tinted glass are interposed in one beam, and the intensity of the light from each beam is made the same. No figure is given.

Denis (J. Biol. Chem. 1921, 47, 27) suggests that turbidimetry by means of a colorimeter may be advantageously substituted for nephelometry in several analytical processes.

For unexpected irregular results with a turbidimeter, *see* König and Krüss (Zeitsch. Nahr.-Genussm. 1904, 7, 587).

In view of the variability that Richards and Wells found when dealing with silver chloride, and in view of the experiences of other authors, it is essential that the peculiarities of each opalescence should be studied and the right conditions for its measurement ascertained, and that a good deal of confirmatory work should be done before relying on nephelometric results, and it is safest to use a standard of a strength not differing much from that of the liquid under examination and similarly prepared; but with these precautions nephelometry is likely to prove extremely useful. H. H. R.

NEPHRITE *v.* Jade.

NEPONITE *v.* Garnierite.

NEROL $C_{10}H_{18}O$ is a terpene alcohol, first isolated by Hesse and Zeitschel (J. pr. Chem. 1902, [ii.] 66, 481) from the neroli oil of orange blossom oil. It is also contained in petit-grain oil (Soden and Zeitschel, Ber. 1903, 36, 265); in Bergamot, Java Cananga, and in French lavender and other ethereal oils (Elze, Chem. Zeit. 1910, 34, 538, 857, 1029; Soden and Treff, Ber. 1904, 37, 1094).

Preparation.—South American petit-grain oil is saponified and then carefully distilled with steam or under reduced pressure. The higher boiling-point fractions contain the nerol together with geraniol and terpineol; the two former are separated from the latter by converting them into their acid phthalic esters. After purifying and saponifying, the mixture is treated with powdered anhydrous calcium chloride with which geraniol gives a solid product, whereas nerol is unaffected and can be washed out with light petroleum (D. R. P. 150495; Soden and Zeitschel, *l.c.*). In a similar manner nerol can be prepared from *Helichrysum angustifolium* and other species of *Helichrysum* from which larger yields are said to be obtained (D. R. P. 209382; Chem. Zentr. 1909, i. 1785). Nerol of the same composition and properties has also been obtained by heating linalool with acetic anhydride and sodium acetate, or with formic acid, or a mixture of sulphuric and acetic acids, the nerol being separated from the resulting product as above (D. R. PP. 165894; 165895; 165896; Zeitschel, Ber. 1906, 39, 1780, 1792).

The nerol obtained by any of the above methods still contains geraniol from which it can be finally purified by treatment with diphenyl carbamide chloride in the presence of pyridine. The geranyl and neryl diphenyl urethanes thus formed are separated by fractional crystallisation from light petroleum.

Neryl diphenyl urethane, m.p. 52°–53°, when treated with an alcoholic solution of potassium hydroxide, yields pure nerol (Soden and Treff, Chem. Zeit. 1903, 27, 897; Ber. 1906, 39, 906).

Properties.—Nerol is a colourless oil, b.p. 226°–227°/755 mm., 125°/25 mm., sp.gr. 0·8813 at 15°, and having a delicate fresh rose smell (Austerweil and Cochin, Compt. rend. 1910, 151, 440), on account of which it has been employed for the manufacture of artificial perfumes (D. R. P. 155287; J. Soc. Chem. Ind. 1903, 819). Nerol has been found to have a toxic action on mice (Hildebrandt, Beitr. Chem. Physiol. Path. 1903, 4, 251). Nerol is probably a space isomeride of geraniol; when oxidised with chromic acid it yields a substance with the odour of methylheptanone, and, probably, citral *b*, mixed with a little citral *a*. Citral *b* when reduced forms nerol. On prolonged shaking nerol forms terpin hydrate (Zeitschel, Ber. 1906, 39, 1780).

Nerol tetrabromide $C_{10}H_{18}OBr_4$, obtained by adding the calculated quantity of bromine to a solution of nerol in chloroform, evaporating and recrystallising from ethyl acetate, forms long, silky needles, m.p. 118°–119° (Soden and Treff, Ber. 1906, 39, 906).

The aliphatic esters of nerol have a similar smell to nerol; the *acetate*, b.p. 93°–94°/3 mm., 134°/25 mm., sp.gr. 0·916 at 15°, saponification number 286·2, and the *formate*, b.p. 119°–121°/25 mm., sp.gr. 0·928 have been prepared (Soden and Zeitschel, *l.c.*; Soden and Treff, *l.c.*).

Nerolidol $C_{10}H_{26}O$ is probably an aliphatic sesquiterpene alcohol. It is contained in neroli and rose oils, and is, possibly, identical with or very similar to farnesol. It forms a colourless oil possessing a faint but permanent pleasant odour, has b.p. 128°–129°/6 mm., 164°–165°/25 mm., 276°–277°/760 mm., sp.gr. 0·880; $[a]_D+13{\cdot}32°$ (Hesse and Zeitschel, *l.c.*), b.p. 149°/4 mm., sp.gr. 0·894 at 15°, $a\pm0°$ (Soden and Treff, Ber. 1904, 37, 1094). It forms an addition product with 6 atoms of bromine.

NEROLI *v.* Oils, essential.

NEROLIN. Trade name for β-naphthol methyl ether.

NEURIDINE, NEURINE *v.* Putrefaction bases and Choline.

NEURODIN *v.* Synthetic drugs.

NEURONAL. Trade name for bromo-diethylacetamide (*v.* Synthetic drugs).

NEUTRAL RED. *Toluylene red* *v.* Azines.

NEUTRAL VIOLET *v.* Azines.

NEVILE AND WINTHER'S ACID. 1-naphthol-4-sulphonic acid.

NEVRALTEIN. Trade name for sodium *p*-phenetidinomethanesulphonate (*v.* Synthetic drugs).

NEVYANSKITE *v.* Iridosmine.

NEW BLUE. *Naphthylene blue, Fast blue 2 B or R, Meldola's blue, New methylene blue* *v.* Oxazine colouring matters.

NEWKIRKITE. A variety of manganite (*q.v.*).

NICCOLITE or **NICKELINE.** Nickel arsenide NiAs, crystallised in the hexagonal system, and containing Ni 43·9 p.c. Small amounts of iron and cobalt are sometimes present; more frequently antimony replaces arsenic, forming a passage, through the variety arite, to breithauptite (NiSb). Crystals are rare, and are usually seen only as the tips of hexagonal pyramids closely clustered together. The massive material sometimes shows a reticulated or a columnar structure. The most characteristic feature of the mineral is its copper-red colour with metallic lustre. It thus presents a striking resemblance to native copper, but it is readily distinguished from this by its greater hardness (H 5–5½), brittleness, and brownish-black streak. On this account the mineral was early known to the old German miners as *Kupfernickel* (copper-nickel), a term meaning worthless as copper, or devil's (Nick's) copper. The element nickel was discovered by A. F. Cronstedt in 1751 in this mineral, from which also it was named. Another characteristic feature, which enables the mineral to be recognised at sight, is the frequent presence of pale green annabergite ($Ni_3As_2O_8,8H_2O$) as an alteration product. The mineral is soluble in hot nitric acid, giving a green solution, which on cooling deposits brilliant octahedra of arsenic trioxide. Sp.gr. 7·3–7·5.

Niccolite occurs somewhat abundantly in the copper-bearing shales of Thuringia (at Mansfeld, Eisleben, and Sangerhausen) and at Riechelsdorf in Hesse; with silver ores at Annaberg and Schneeberg in Saxony, and at Joachimsthal in Bohemia; with native silver in the Cobalt district in Ontario; and it has been occasionally found in Cornwall and Scotland, *e.g.* with pyrrhotite in mica-diorite at Talnotry near Newton Stewart in Kirkcudbrightshire. The mineral has been mined, especially in Thuringia and Spain, as a source of nickel and for the manufacture of white arsenic. L. J. S.

NICHOLSON'S BLUE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

NICHROME. An alloy usually containing Ni 58–62, Fe 23–26, Cr 8–14, Mn, Zn, Si 0·5–2·0, and Co 0·2–1·0 p.c. *See* NICKEL.

NICKEL. At.wt. 58·68;[1] sym. Ni.

Nickel consists of two isotopes of masses 58 and 60 in the proportion of 2 : 1. This gives a value 58·67 which agrees closely with the accepted number.

History.—The discovery of this metal is attributed to Cronstedt (1751–1754), who found it in *Kupfernickel* (false-copper), a term applied to the mineral by the miners of Saxony, because, although its appearance resembled that of copper ores, they were unable to extract copper from it. Bergman first prepared pure nickel in 1775, but, alloyed with copper and zinc, the metal had been used by the Chinese in very early times.

Occurrence.—Nickel is widely diffused in nature, and has been very frequently detected in igneous rocks, especially magnesian varieties, in which it is generally associated with chromium. It is found native, alloyed with iron, in meteorites and in the terrestrial minerals *awaruite* and *josephinite*, which contain 60 p.c. or even more metallic nickel. Numerous compounds exist in nature, but the following are the most important ore-minerals:—

Pentlandite	(Fe, Ni)S
Millerite	NiS
Niccolite (Kupfernickel)	NiAs
Chloanthite	$NiAs_2$
Gersdorffite	NiAsS
Breithauptite	NiSb
Annabergite	$Ni_3As_2O_8+Aq.$
Garnierite	$H_2(Ni,Mg)SiO_4+Aq.$ (variable).

The chief sources of nickel are, in relation to the world's production: (1) the ores of Sudbury, Ontario, which are chiefly *pyrrhotite* (magnetic iron pyrites) containing *pentlandite* and *chalcopyrite* (copper pyrites), in a matrix of norite; and (2) those of New Caledonia, in which the nickel exists as *garnierite*, a variable mixture of nickel silicates, magnesian compounds, and free silica.

The Ontario ores yield nearly 80 p.c. of the world's output. During 1916, over 1½ million tons were smelted with the production of between 40,000 and 50,000 tons nickel and about half as much copper. Nickeliferous pyrrhotite ore is also worked in Norway (accounting for the production of from 500 to 1000 tons nickel per annum), and has been mined to a much smaller extent in Pennsylvania, Tasmania, Sweden, Italy, South Africa and elsewhere. Silicate ores, similar to garnierite, occur also in Greece, Madagascar, North Carolina and elsewhere, but the output from these sources is commercially unimportant. The arsenical ores (chiefly arsenides) usually contain both nickel and cobalt, and are worked in Cobalt, Ontario, as well as in Saxony, Bohemia, France and elsewhere.

The production of both Ontario and New Caledonia is increasing, although the former is probably three or four times greater than the latter. The pyrrhotite ores of Sudbury, whose reserves are estimated to be about 140 million tons proven ore, contain an average of from about 2 to 3 p.c. nickel, 1 to 1½ p.c. copper, and 40 p.c. iron. The New Caledonian ores contain about 5 p.c. nickel, about ½ p.c. cobalt, and practically no copper. Cobalt is invariably present in nickel ores although frequently in small amount; the Sudbury pyrrhotite contains only a fraction of 1 per cent. Silver, gold, and the platinum group metals are present in the Sudbury ores in small but important amounts, the average being probably about: gold 0·01, silver 0·2, platinum metals 0·01–0·02 ounces per short ton.

Extraction.—The first stage in the extraction of nickel from its ores is, almost invariably, that of smelting the crude ore, whereby the nickel, and when present, the copper, becomes concentrated from the gangue of the ore, in the form of a matte composed of the lower sulphides of the metals. In Canada most of the ore is smelted locally and the matte exported hitherto to the United States or Europe to be refined. Steps are now being taken to carry out the refining within the Dominion. Smelting is also carried out in New Caledonia, but ore is also shipped to Europe in large quantities for treatment in France and England. A considerable amount of experimental work has been carried out with a view to the enrichment of ores by methods of water concentration and oil flotation, but, at the present time, with the exception of hand picking, practically the whole of the nickel ore mined is smelted direct to a matte. The practice in Canada, and elsewhere where the ore consists of a sulphide, consists of three operations: (*a*) roasting for the removal of a portion of the sulphur; (*b*) smelting for the production of a low-grade, highly ferruginous matte; (*c*) the removal of the iron and a large proportion of the sulphur in a Bessemer converter for the production of a high-grade matte, and (*d*) the refining of the nickel-copper matte, *i.e.* conversion into metal.

(*a*) In Canada, heap roasting is still largely practised, the Canadian Copper Company, the largest operating concern in Canada, has about 250,000 tons of ore roasting at one time, and roasts over 60 p.c. of its ore in this manner to a content of from 10–12 p.c. sulphur. Each heap contains about 2500 tons of ore laid on a foundation of about 12 or 18 inches of wood, with flues about 10 feet apart. Coarse ore is first piled on the wood, followed by layers of medium size and fines which cover the entire heap and regulates the rate of combustion; the roasting is completed in three or four months. Only a comparatively small proportion of the fines can be roasted in the heaps, the remainder is roasted in mechanical furnaces of the Wedge type, or by the Dwight-Lloyd sintering process.

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[1] No difference has been observed in the atomic weight of terrestrial and meteoric nickel.

(*b*) The smelting of nickel ores of the Sudbury type is similar to that of smelting pyritic copper ore, that is to say, sufficient sulphur must remain in the roasted ore to combine as sulphides with the nickel, copper, and a portion of the iron to form matte. The roasted ore will contain from 2½ to 4 p.c. Ni, 1½–2 p.c. Cu, 32–40 p.c. iron, and 9–11 p.c. S, and it is the usual practice for a portion of the furnace charge to consist of raw ore. The smelting is carried out in blast or reverberatory furnaces, the Canadian Copper Company using both (the former for lump ore and the latter for fines) and the Mond Nickel Company only blast furnaces. The water-jacketed blast furnaces of the Canadian Copper Company measure 50″×204″ at the tuyeres, and 19′ from the hearth to the charging level, and have a smelting capacity of about 400 tons of ore per day of 24 hours. Those of the Mond Nickel Company measure 50″×240″ and have a capacity of about 420 tons of ore. The charge consists of roasted ore, or roasted and raw ore mixed to the correct proportion of sulphur, slag and scrap from the converters, limestone and quartz, and about 11 p.c. of coke to the charge. During the smelting, the greater part of the iron passes into the slag, and a portion of the sulphur in the charge oxidises and volatilises as SO_2, while the nickel, copper and the remainder of the iron become sulphides, and form the matte. The molten products flow continuously into the settlers lined with chrome bricks; the slag, with a sp.gr. of about 3·7, overflows into 25-ton pots, while the matte, with a sp.gr. of 4·6–4·8, settles to the bottom and is tapped off at intervals into 7-ton ladles, which are carried by rail to the converter building.

The low grade, or raw, matte thus produced represents a concentration of about 100 ore to 23 matte, a higher concentration is not found to be economical owing to increased losses of metal in the slag. The matte contains an average of 20–25 p.c. nickel *plus* copper, the ratio of nickel to copper being between 1¼ and 2¼ to 1, according to the relative amounts present in the original ore. The slag averages 0·16 p.c. copper and 0·32 p.c. nickel and carries about 9 p.c. of the original nickel-copper content. This loss is found to increase if a greater concentration of matte is attempted in the blast furnace. Reverberatory furnaces (coal-dust fired) are used by the Canadian Copper Company for smelting the fine ore and flue dust. The matte produced is similar, but the metal recovery is not so high as in the blast furnace. The Mond Nickel Company dispenses with the use of reverberatory furnaces, by sintering the fines in Dwight-Lloyd furnaces and adding the partly de-sulphurised sinter to the blast furnace charge. The treatment of the New Caledonian garnierite ores is carried out on the same principle as that for Sudbury and other pyritic ores except that, there being practically no sulphur in the ores to form matte, sulphur is added in the form of gypsum to the blast furnace charge. The ore is ground and mixed with limestone, gypsum, and coal or coke and briquetted. The raw matte contains about 45 p.c. Ni, 25–30 p.c. Fe, and 16–20 p.c. S, and practically no copper or precious metals.

(*c*) The enrichment of the matte is best carried out in the Bessemer converter. Unlike copper, nickel or nickel-copper matte cannot be reduced to metal in the converter, as there is no similar reaction between nickel sulphide and nickel oxide. Bessemerisation consists in blowing air through the molten matte, and is carried out solely with a view to the oxidation and removal of the iron as silicate and the production of a high-grade matte. The earlier practice in Sudbury was to use 'acid' converters, so called because the converter lining was composed of silicious matter (quartz and clay) which was acted upon by the FeO, with the formation of an iron silicate slag. Latterly, basic converters, lined with magnesite brick, have been substituted, and the silicious matter is added on the top of the matte as required, thus avoiding the necessity for frequent relining. The Canadian Copper Company's converters are of the horizontal type, 37′ 2″ long by 10′ diameter, outside measurement. The whole operation requires about 50 hours to convert a full charge of about 400 tons of raw matte into about 100 tons of refined matte containing as nearly as possible 80 p.c. nickel *plus* copper (say 53½ Ni and 26½ Cu) and 20 p.c. sulphur and about ½ p.c. iron. In the process of oxidising, practically the whole of the iron, and a small amount of the nickel-copper is also oxidised and enters the slag, which is returned to the blast furnace. The slag varies in composition during the 'blow,' the average containing about 1 p.c. Cu and 3 p.c. Ni. The New Caledonian blast furnace matte is bessemerised in a similar manner, but usually in smaller converters. The refined matte contains from 65–75 p.c. Ni, the balance being sulphur.

(*d*) *Nickel refining.*—For the production of metallic nickel from refined nickel-copper matte, there are three standard methods in use, viz. (1) the Orford, (2) the Mond, and (3) the electrolytic. (1) The Orford process consists of smelting the matte with sodium sulphate and carbon (producing sodium sulphide) in reverberatory furnaces. The fused mass separates into two layers which are tapped separately. The upper layer, known as 'tops,' is composed of double sulphides of sodium and copper containing a small proportion of nickel, while the lower, or 'bottoms,' consists of a nickel matte, much richer in nickel and poorer in copper. By repetitions of the operation, concentration of the greater part of the nickel is effected. The final bottoms, still containing a small percentage of copper, are ground, roasted with salt in a reverberatory furnace, and leached with water. The solution contains most of the remaining copper and a portion of the silver and platinum group metals. The residue consists of nickel oxide, which is reduced in reverberatory furnaces to metal containing about 99 p.c. Ni, including a little Co. The working costs of the Orford process are low, but it is believed that the losses of nickel and copper are greater than in either of the other two processes, and but a small proportion of the precious metals is recovered. (2) The Mond process (Eng. Pat. 23665, Dec. 10, 1895) depends upon the fact that when carbon monoxide is passed over metallic nickel at 50° C. a carbonyl ($Ni(CO)_4$) is formed which, on being heated to 150°C., is again decomposed into metallic nickel and carbon monoxide. The Mond Nickel Company produces a matte in Ontario averaging 41 p.c. nickel and 41 p.c. copper, which is shipped to Wales for treatment. The matte is finely ground, roasted, and leached with 10 p.c. sulphuric acid, which extracts about two-thirds of the copper. The residue is reduced to metal by water gas or producer gas rich in hydrogen, in specially constructed reduction towers, at a temperature not exceeding 350°C., in order that the small amount of iron present shall not be reduced beyond the ferrous state. The finely divided nickel is subjected to the action of carbon monoxide in similar towers at a temperature of between 50° and 80°C., when the volatile carbonyl passes away to the decomposer. The operation is not completed in one passage; the residue is returned to the reducer, and then to the volatiliser, circulating in this manner for from 7 to 15 days. About 70 p.c. of the nickel is thus removed, and the residue, which is similar in composition to the original roasted matte, is smelted with gypsum and carbon for the production of a matte similar to the original 80 p.c. matte. This is re-treated and the final residues are sold, principally for their content of platinum and palladium, although they contain also small amounts of iridium, rhodium, gold and silver. The volatilised nickel carbonyl is decomposed at a temperature of about 200°C. in a tower containing granules or small pellets of nickel kept in motion to prevent cohesion. The gas passes upwards through the interstices between these pellets, on to which nickel is deposited as the nickel carbonyl is decomposed. The pellets are automatically removed, screened, and the smaller size returned to the top of the tower, while those from ⅛″ to ⅜″ are sold. The purity of the nickel is high, 99·8 p.c. or better, with a little iron and minute quantities of sulphur and carbon. The copper sulphate, obtained by leaching the roasted matte with sulphuric acid, is crystallised and sold as such, and the nickel sulphate is recovered from the mother liquors. The Mond process is carried out to-day in substantially the same manner as was fully described by Roberts Austen (Proc. Inst. Civ. Eng. 135, 29). (3) A number of electrolytic methods for refining have been tried from time to time in Canada and the United States (notably those of C. Hoepfner, Eng. Pat. 11307, 1894, and H. A. Frasch, U.S. Pat. 469, 439–469, 442, Mar. 5, 1901), but, for various reasons, have been given up. Latterly the British-America Nickel Corporation has adopted V. M. Hybinette's process (Eng. Pat. 13355, 1914) for the refining of nickel in the new plant now being installed in Ontario. By this process, already successfully operated in Norway on poorer ores than those of Sudbury, the nickel is deposited electrolytically from soluble anodes made from partly roasted nickel-copper matte. The bessemerised matte produced in Norway contains an average of 47 p.c. Ni and 33 p.c. Cu. It is roasted to remove the bulk of the sulphur and leached with 10 p.c. sulphuric acid, which dissolves a large proportion of the copper but very little nickel. The residue is melted and cast into anodes containing about 65 p.c. Ni, 3–8 p.c. sulphur, about 30 p.c. copper, and a trace of iron. The electrolyte contains 45 grammes Ni and from 3–5 milligrammes Cu per litre. After circulation, it contains from 2–3 grammes Cu per litre and is passed over waste anodes, when the copper is precipitated and nickel regenerated. The nickel cathodes are made of iron plates rubbed over with a thin wash of water and graphite. The deposited nickel is sold in sheets without remelting. The metal is guaranteed 99 p.c. and contains not more than 0·1 p.c. Cu and an average of 0·5 p.c. iron. The precious metals are recovered from the anode slime. The copper is similarly deposited electrolytically on sheet copper cathodes and the precious metals recovered in the slime. The percentage recovery of nickel, copper, and precious metals is high.

Other processes suggested for the treatment of oxidised ores include the direct production of ferro-nickel, extraction from the ore after chloridising and sulphatising roast, &c., but none are, to any extent, in commercial use at the present time. Large quantities of a natural alloy of nickel and copper, known as *monel metal*, are now produced from Sudbury ores by the direct smelting of roasted matte, from which a small proportion of the copper has been removed by the first stage of the Orford process. Its average composition is about 68 p.c. nickel, 30 p.c. copper, and 1½ p.c. iron; its properties are referred to later in this article. The proposal has been recently revived in Canada and elsewhere to smelt the old slags, hitherto thrown to waste, for the production of a pig iron low in nickel.

The production of nickel from arsenical ores, such as those containing niccolite (kupfernickel) and chloranthite, is carried out on a relatively small scale. The ores commonly contain also cobalt, iron, and other metallic sulphides, and are roasted and smelted for the production of a speiss composed chiefly of nickel arsenide. The speiss is subjected to repeated oxidising and reducing roasts to drive off the arsenic, and finally the nickel oxide is reduced with carbon. Wet methods are employed for the separation of the cobalt, *v.* COBALT, Vol. II.

Properties of Nickel.—Nickel is a lustrous silver-white metal having a slight steel-grey tinge, which is very noticeable when it is compared with silver. It is sufficiently hard to take a fine polish. Nickel is magnetic at ordinary temperatures, but, like iron, becomes non-magnetic at high temperatures, the transition occurring between 340° and 360°C. Its specific gravity is 8·35, increasing to 8·6–8·9 by mechanical treatment. Its hardness is stated to be 3·5 of Moh's scale (Copaux, Compt. rend. 1905, 140, 657) and its melting-point is 1452°C. (Henning, Zeitsch. Electrochem. 1913, 19, 185; Dana and Foote, Trans. Faraday Soc. 1920, 15, 186;

1452, 3; Day and Sosman, Phys. Rev. 1907. 125, 1; Acad. Sci. 1913, 3, 371) and its specific heat 0·109. The electrical conductivity of nickel is about 12·9 compared with silver at 100; its specific resistance is 6·4 microhms/c.c. and its breaking stress 42 kilos. per sq. mm. (Copaux, *l.c.*). Nickel is malleable and ductile, and can be rolled into sheets 0·028 mm. thick and drawn into wire 0·014 mm. diameter. Its malleability and ductility are diminished by the presence of carbon, manganese, arsenic, sulphur or nickel oxide. At a white heat it can be welded to itself, to iron, and to various alloys.

Nickel may be distilled in the electric furnace, the distillate having the same properties as the finely divided metal. It is not so volatile as manganese, but more so than iron or chromium (Moissan. Compt. rend. 1906, 142, 425). Its boiling-point is 2490°/30 mm.

The metal does not readily tarnish in the air at ordinary temperatures, but becomes coated with a greenish coloured oxide at a red heat. When heated, nickel wire burns in oxygen; it also becomes incandescent in nitric oxide at 200° and is pyrophoric when prepared by hydrogen reduction. It decomposes steam slowly at a red heat. Acetic, citric, tartaric and oxalic acids have little or no action on nickel unless they are left in contact for a long time. Fused caustic alkalis have no action and it is unaffected by fresh or sea water. It dissolves slowly in dilute sulphuric and hydrochloric acids, rapidly in nitric acid or *aqua-regia*. In contact with concentrated nitric acid, it becomes passive like iron; when dropped into fuming nitric acid it may be violently attacked, may become passive, or may be disintegrated to a grey magnetic powder (Holles, Proc. Camb. Phil. Soc. 1904, 12, 253). Hydrogen is occluded by nickel at temperatures above 200° C., in quantity increasing with the temperature, but very different values have been obtained for the actual amount (*cf.* Bayer and Altmayer, Ber. 1908, 41, 3062; and Sieverts, Zeitsch. physikal. Chem. 1907, 60, 129).

Molten nickel absorbs carbon monoxide, given off on cooling, which produces unsound castings full of blow-holes. It has the power of dissolving its monoxide, forming a eutectic similar to that formed by copper with cuprous oxide, and with the same result, *i.e.* brittleness of the metal. Fleitmann (Ber. 1879. 12, 454) first suggested the addition of a small amount of magnesium to the molten metal, by which means the nickel oxide is reduced and perfectly sound castings obtained. Aluminium is said to act in a similar manner, and manganese is also stated to act as a purifier and to improve the quality of the metal. Nickel may be deposited as a metallic layer on other metals by electrolysing a solution of nickel, usually the double sulphate $NiSO_4(NH_4)_2SO_4,6H_2O$. The deposited nickel is hard and will take a brilliant polish.

The nickel of commerce, with the exception of that manufactured by the Mond process, is generally impure. It commonly contains only about 98-98½ p.c. nickel, often as much as 1 p.c. cobalt, 0·3-0·6 p.c. iron, a little copper, silicon and magnesium. Arsenic, sulphur and nickel oxide are also occasionally present, causing brittleness in the metal and diminishing or destroying its malleability and ductility. Even 0·1 p.c. of arsenic or sulphur is injurious. The presence of iron hardens nickel, 1 p.c. rendering the metal unsuitable for the best qualities of nickel silver. With 1 p.c. carbon, nickel is brittle, but with a higher percentage it becomes tough. Although extreme purity is essential in some cases, the less pure nickel is equally suitable for many purposes, and is occasionally preferred on account of greater ease in alloying. Nickel is commonly sold in the form of cubes, in discs, known as 'rondelles,' granules, and in 'plaquettes'; also shot of various standard sizes prepared by the Mond Nickel Company. (For methods for determining nickel, *see* Bradley and Ibbotson's Analysis of Steel Works Materials; also Spring, Chem. News, 104, 58; Ibbotson, Chem. News, 104, 224; Schoeller and Powell, Analyst, 1917, 62, 189.)

Uses of Nickel.—The report of the Royal Ontario Nickel Commission (1917) states that no actual statistics are available, but gives the following approximate estimates of the relative quantities of nickel used annually for certain specific purposes: *Coinage*, not over 500 tons. *Electro-plating*, metallic nickel and its salts, equivalent to about 500 tons of metallic nickel, is consumed in England. *Nickel-silver* and other alloys not containing iron or that used for coinage, between 500 and 3000 tons in England. *Steel* making probably 75 p.c. of the whole nickel production (war time) and 60 p.c. under normal conditions. In England about 2750 tons, or about 45 p.c. of the whole English consumption, is normally used in steel. The Imperial Institute states that 4700 tons was used in the steel industry during 1914, and that it accounted for about 70 p.c. of the total nickel used in England. The use of nickel for coins of low denomination is increasing; most countries use an alloy of 25 p.c. nickel and 75 p.c. copper, but the pure metal is also used: its hardness causes it to be of special value for coinage on account of both its durability and difficulty of counterfeiting. It is used to an increasing extent in the manufacture of laboratory appliances such as crucibles and basins (which may be used for boiling with caustic alkalis or alkaline carbonates and for fusing minerals and salts with caustic alkalis or nitrates of the alkalis), water-baths, spatulas, tongs, &c. For some larger scale chemical operations, iron vessels lined with nickel are employed. In the pure form, metallic nickel is manufactured into sheets which are stamped into watch cases, cooking utensils, and similar articles. It is drawn into wire for use for sparking-plugs and leading-in wires. Nickel is largely used as a catalyst, notably in the hydrogenation of oils.

Alloys.—Nickel is capable of alloying with all the common metals, and, in addition to its use in steel, it enters into the composition of a large variety of non-ferrous alloys chiefly known in commerce as *cupro-nickel*, *nickel-silver*, *German-silver*, *nickel-bronze*, &c.

The principal characteristics of nickel steel (containing from 2 p.c. and upwards Ni, usually about 3½ p.c.) is its high elastic and tensile strength compared with mild steel, and for this reason it is rapidly replacing ordinary structural steel for many purposes such as bridge construction, &c. It is also used for special locomotive and engineering forgings, electric railway gears, crankshafts, for parts of motor-cars, aeroplanes, and it has also proved of special value for armour plate, heavy ordnance, and armour-piercing projectiles. (For the effect of nickel in steel, *see* Sir R. Hadfield, Proc. Inst. Civ. Eng. 138, 1-125.) *Invar* is an alloy of iron containing 36 p.c. nickel, 0·5 p.c. manganese, and 0·5 p.c. carbon. It has practically no coefficient of expansion between −100° and +150° C., and for this reason is of special value for clock pendulums, surveying tapes, philosophical instruments, &c. It melts at 1425°C. and can be forged, drawn and worked readily, and has a high resistance to corrosion. *Platinite* and other high nickel steels are used for special purposes such as electrical resistances, &c.

The non-ferrous alloys have a wide application for domestic and engineering purposes; the addition of nickel hardens and toughens many of the common metals and alloys. With 25 p.c. nickel, copper-nickel alloys are white: with less nickel they show a reddish tint. *Monel metal* is, as already stated, a natural alloy, produced by direct smelting of the ore. It contains about 67 p.c. nickel, 28 p.c. copper, and 5 p.c. manganese and iron. It takes a brilliant polish and is remarkable for its resistance to corrosion and high tensile strength. Its melting-point is 1360°C. and sp.gr. (cast) is 8·87. It is made in the form of sheets, rods, wire and castings, and is largely used for propeller blades, valves, castings for oil stills, tie rods, ore dressing screens, filter cloth, &c. (*see also* Engineering, 1918, 106, 451). *Cupro-nickel* contains 80 p.c. copper and 20 p.c. nickel. It melts at 1190°C. and is used for bullet jackets and other munitions of war. The alloys of the *nickel-silver* (*German-silver*) group usually contain about 55-60 p.c. copper, 15-20 p.c. nickel, and 20-30 p.c. zinc, but the lower grades contain as little as 7 p.c. nickel (McWilliam and Barclay, J. Inst. Metals, 1911, 5, 214). The alloys are not definite compounds, but consist of a homogeneous solid solution. They are white, ductile and tough and not readily corroded, and may be rolled, spun, stamped and drawn. *Packfong* is the name of an old Chinese alloy of copper, zinc, and nickel; other alloys having the same constituents, but widely varying in quantities, are known in commerce under the names *argentan, Potosi silver, electrum,* and, in France, *maillechort.*

A number of nickel-copper alloys are made for use as electrical resistances, e.g. *constantan* and *eureka,* containing 60 p.c. copper and 40 p.c. nickel; *platinoid,* stated to contain about 2 p.c. tungsten; and *manganin,* containing 84 p.c. copper, 4 p.c. nickel, and 12 p.c. manganese. *Nichrome* resistance wire is an alloy of 60 p.c. chromium and 40 p.c. nickel. Constantan is used for thermo-electric couples, as is also an alloy of nickel 90 p.c. and chromium 10 p.c. For a full account of the nickel industry, including ore deposits of the world, *see* the Report of the Royal Ontario Nickel Commission, published in 1917 by the Ontario Government, Toronto.

For an account of the growth of the nickel industry since 1910, *see* Mathewson, Jour. Soc. Chem. Ind. 1918, 37, 53.

Colloidal solutions of nickel can be prepared by the reduction of solutions or suspensions of nickel salts in glycerol containing gelatin or gum arabic as a protective colloid (Kelber, Ber 1917, 50, 1509). The reducing agents may be hydrazine hydrate, formaldehyde, hydroxylamine or hypophosphorous acid. The colloidal solution is unaltered by air and is miscible with alcohol.

Oxides of nickel. The chief oxides of nickel are the monoxide NiO and the sesquioxide Ni_2O_3.

Nickel monoxide NiO occurs native as *bunsenite,* and may be prepared by strongly heating the hydroxide $Ni(OH)_2$, carbonate $NiCO_3$, or nitrate $Ni(NO_3)_2$. It is a green crystalline powder, which turns yellow on heating. It is easily reduced to the metal when heated in hydrogen. The *hydroxide* $(NiOH)_2$ is formed as an apple-green precipitate, when a nickel salt is treated with alkali hydroxide.

The salts of nickel are derived from the monoxide. They are in general yellow when anhydrous, emerald-green when hydrated or in solution.

Nickel sesquioxide Ni_2O_3 is a black powder obtained by gently heating the nitrate or carbonate in air. It is decomposed by heat, and is probably nickelous nickelite $NiO{\cdot}NiO_2$.

Nickel trihydroxide $Ni(OH)_3$ is obtained as a black precipitate when a nickel salt is warmed with alkali hypochlorite or chlorine passed through the hydroxide $Ni(OH)_2$ suspended in water. According to Bellucci and Clavari, however, this precipitate is the hydrated dioxide $NiO_2{\cdot}xH_2O$ (Gazz. chim. ital. 1905, 14, ii. 234; Atti R. Accad. Lincei, 1907, [v.] 16, i. 647).

The *peroxide* NiO_2 is obtained in a hydrated form by the action of hydrogen peroxide on nickel salts (Pellini and Meneghini, Zeitsch. anorg. Chem. 1908, 60, 178), and an oxide regarded as NiO_4 was obtained by Hollard (Compt. rend. 1903, 136, 229).

According to Sabatier and Espil (Compt. rend. 1914, 158, 668) a suboxide Ni_4O (?) probably exists. According to Wöhler and Balz (Zeitsch. Elektrochem. 1921, 27, 406), this is a mixture of NiO and metal.

Nickel carbonyl $Ni(CO)_4$. When carbon monoxide is passed over reduced nickel at 30°–80°, best at about 45°, combination occurs, and a volatile carbonyl is formed (Mond, Langer and Quincke, Chem. Soc. Trans. 1890, 749). It is a colourless liquid, boiling at 43·2° and solidifying at −25°; its sp.gr. is 1·3185 at 17°. At 50° it has the normal vapour density. The carbonyl is soluble in organic media; its vapour is very poisonous. For its reactions, see Dewar and Jones, *ibid.* 1904, 203; Proc. Roy. Soc. 1903, 71, 427; and *v.* CARBONYLS, Vol. II. p. 86.

Nickel arsenide NiAs occurs as *kupfernickel* (*v. supra*). The *phosphide* Ni_2P is obtained in grey needles when nickel and phosphorus are heated in the electric furnace (Maronneau, Compt. rend. 1900, 130, 656; *cf.* Granger, *ibid.* 1896, 122, 1484; 1896, 123, 176).

Nickel nitride Ni_3N_2 is obtained by dropping a mixture of nickelous oxide and cyanide between carbon electrodes in an atmosphere of nitrogen (Vournasos, Compt. rend. 1919, 168, 889).

Nickel boride NiB is prepared in the electric furnace, and forms brilliant prismatic crystals of sp.gr. 7·39 (Moissan, Compt. rend. 1896, 122, 424). It is decomposed when fused with alkali.

Nickel silicide Ni_2Si is prepared by heating an excess of nickel with silicon in the electric furnace until the greater part of the metal has been volatilised; and then dissolving away the remaining metal with dilute nitric acid. It is a steel-grey, metallic-looking powder of sp.gr. 7·2, and is attacked by *aqua regia* and by hydrofluoric acid (Vigouroux, Compt. rend. 1895, 121, 686).

Nickel bromide $NiBr_2$ is produced when finely divided nickel is heated in bromine vapour or by the action in the cold of an ethereal solution of bromine on the metal. It sublimes in golden scales. The bromide is very hygroscopic, and forms a trihydrate $NiBr_2,3H_2O$. The accepted equivalent of nickel rests largely upon the results obtained by Richards and Cushmann (Zeitsch. anorg. Chem. 1898, 16, 167; 1899, 20, 352) in their analyses of anhydrous nickel bromide.

Nickel carbonate $NiCO_3$ is obtained by heating a solution of nickel chloride with calcium carbonate at 150°. It forms pale-green, microscopic rhombohedra. A hexahydrate $NiCO_3,6H_2O$ is produced by mixing nickel nitrate solution with sodium bicarbonate and saturating the cold solution with carbon dioxide. It readily loses water. The pale green precipitates obtained by adding alkali carbonate to a nickel salt are basic carbonates of variable composition.

Nickel chloride $NiCl_2$ is formed when finely divided nickel is warmed in chlorine. It can be sublimed, and forms golden scales. It dissolves in water with the evolution of heat, and a green hexahydrate $NiCl_2,6H_2O$ can be crystallised out from the solution. The anhydrous chloride readily absorbs ammonia, forming an almost white compound $NiCl_2,6NH_3$, which dissolves easily in water. Nickel chloride is soluble in alcohol.

Nickel cyanide $Ni(CN)_2$ is obtained as an apple-green precipitate by adding potassium cyanide to a solution of a nickel salt. It is easily soluble in excess of potassium cyanide, and from the solution the salt K_2NiCy_4 can be crystallised. This salt is readily decomposed by dilute acids; a red potassium nickelocyanide K_2NiCy_3 is also known. It can be oxidised to the normal yellow nickelocyanide K_2NiCy_4 by atmospheric oxygen, water, or by hydrogen peroxide (Bellucci, Gazz. 1919, 49, ii. 70).

Nickel fluoride NiF_2 forms green prisms (Poulenc, Compt. rend. 1892, 114, 1426); it is soluble in water and forms a trihydrate $NiF_2,3H_2$.

Nickel iodide NiI_2 forms black scales; the hexahydrate $NiI_2,6H_2O$ is a bluish-green, very hygroscopic crystalline substance.

Nickel nitrate $Ni(NO_3)_2,6H_2O$ is a green salt which crystallises in monoclinic tablets. It dissolves in twice its weight of cold water and is also soluble in alcohol. Tri- and mono-hydrates are also known.

Nickel nitrite $Ni(NO_2)_2$ is of little importance itself. It forms a double salt $Ni(NO_2)_2{\cdot}4KNO_2$ which is easily soluble in water, and a triple nitrite $2KNO_2{\cdot}Ca(NO_2)_2{\cdot}Ni(NO_2)_2$, which is a yellow crystalline substance only sparingly soluble in water. Similar salts are known with barium and strontium, and hence the alkaline earth metals must be absent when nickel and cobalt are to be separated by the cobaltinitrite method.

Nickel sulphate $NiSO_4$ is formed in solution when nickel, or the hydroxide or carbonate is dissolved in dilute sulphuric acid. At ordinary temperatures the salt crystallises as the green heptahydrate $NiSO_4,7H_2O$, isomorphous with magnesium sulphate. At 50°–70° the hexahydrate $NiSO_4,6H_2O$ separates in monoclinic crystals, and a hydrate of the same composition separates at ordinary temperatures from acid solutions, but the crystals are tetragonal pyramids.

The hydrated sulphate loses water at 100°, forming the monohydrate $NiSO_4,H_2O$, and at 280° the yellow anhydrous sulphate is left. The latter absorbs ammonia, forming a pale violet powder of the composition $NiSO_4{\cdot}6HN_3$. The compound $NiSO_4{\cdot}4NH_3,2H_2O$ crystallises in dark-blue tetragonal prisms from concentrated solutions of the sulphate in ammonia.

The solubility of nickel sulphate in water, expressed as parts of the anhydrous salt per hundred parts of water, is as follows:—

Temp.	2°	16°	23°	41°	50°	60°	70°
$NiSO_4$	30·4	37·4	41·0	49·1	52·0	57·2	61·9

Nickel sulphate forms numerous double sulphates with the sulphates of other metals. Of these, the most important is *nickel ammonium sulphate* $NiSO_4{\cdot}(NH_4)_2SO_4,6H_2O$, which is largely used in the process of nickel plating and in other processes in which a salt of nickel is employed. It is obtained by dissolving either nickel or nickel monoxide in sulphuric acid, and adding ammonium sulphate to the concentrated acid solution. It is purified by recrystallisation and forms short, monoclinic prisms. The solubility, expressed as parts of $NiSO_4{\cdot}(NH_4)_2SO_4$ per hundred parts of water, is as follows:—

Temp.	3·5°	16°	20°	30°	40°	50°	68°	85°
Salt	1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6

Nickel monosulphide NiS occurs in nature as *millerite*, sometimes in brass-yellow rhombohedra, but usually in capillary crystals. It is obtained in a black, hydrated form when a nickel salt is precipitated by ammonium sulphide. For its behaviour towards acids, *cf.* Thiel and Gessner, Z. anorg. Chem. 1914, 86, 1. For the subsulphide Ni_2S, *v.* Mourlot, Compt. rend. 1897, 124, 768, and for the sesquisulphide, *v.* Dewar and Jones, Chem. Soc. Trans. 1904, 211.

Detection and estimation. Nickel salts colour the borax bead red in the oxidising flame. The sulphide is black, and cannot be precipitated in the presence of mineral acids, but when once precipitated, it dissolves very slowly in dilute hydrochloric acid.

Nickel may be estimated as the metal, as the monoxide, as nickel dimethyl glyoximate or as nickel dicyanodiamidine; it may also be estimated volumetrically (*cf.* Holluta, Monatsh. Chem. 1919, 40, 281; J. Soc. Chem. Ind. 1919, 38, 964, A). For details of these methods, and for the separation of nickel from other metals, *v.* ANALYSIS. W. G. W.

NICKEL-SILVER *v.* NICKEL.

NICOTIDINE *v.* BONE OIL.

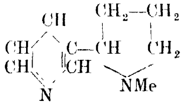
NICOTINE $C_{10}H_{14}N_2$, a liquid, volatile alkaloid, occurring in tobacco (*Nicotiana Tabacum* [Linn.]) as malate and citrate, together with several other alkaloids of comparatively little importance, *e.g.* *nicoteine* $C_{10}H_{12}N_2$, b.p. 266°, liquid; *nicotimine* $C_{10}H_{14}N_2$, b.p. 250°–255°, liquid; *nicotelline* $C_{10}H_8N_2$, m.p. 148°, prismatic needles. Nicotine also occurs in *Duboisia Hopwoodii* (F. Muell.) (Rothera, Bio-Chem. J. 1910, 5, 193), from which it was isolated under the name 'piturine' (*see* Petit, Pharm. J. 1878–1879, [iii.] 9, 819). Tobacco contains, as a rule, from 1 to 8 p.c. of nicotine, but by far the greater proportion of commercial tobacco contains not more than 4 p.c. (*v.* TOBACCO).

Preparation. Nicotine and tobacco extract are now largely used as insecticides, and a considerable industry has sprung up in the last few years in the manufacture of these products. For these purposes tobacco leaf midribs and waste tobacco are largely used, as well as the liquors obtained in the manufacture of chewing tobacco. The tobacco is extracted with water usually in some form of continuous extraction apparatus, and this liquor, or that produced in making chewing tobacco, is concentrated to form tobacco extract. From the latter crude nicotine can be obtained by adding lime or soda solution and steam-distilling, the distillate being extracted with ether.

Estimation. The process generally employed for this purpose is that of Kissling (Zeitsch. anal. Chem. 1882, 21, 64; 1883, 22, 199; Chem. Zeit. 1911, 35, 98, 200; 1916, 40, 594), which has been modified in various ways. The following form of this process is stated to give good results: 20 grms. of powdered tobacco, dried at a temperature not exceeding 60°, is ground up in a mortar with 10 c.c. of 55 p.c. alcohol containing 0·6 grm. of sodium hydroxide and extracted with ether in a Soxhlet apparatus until exhausted (usually in 3 hours). The solvent is distilled off and the residue mixed with 50 c.c. of 0·4 p.c. soda solution and steam-distilled, and the distillate (which generally need not exceed 400 c.c.) titrated with $\frac{1}{10}$ N-sulphuric acid in presence of rosolic acid. For extracts the same process may be used, alkali being added to the extract and the mixture steam-distilled. For a critical examination of this and other methods, *see* Rasmussen (Zeit. anal. Chem. 1916, 55, 81–131). In addition to Kissler's method (above) and that of Koenig (Chem. Zeit. 1911, 35, 521), Rasmussen favours the precipitation as silicotungstate (Bertrand and Javillier, Bull. Soc. chim. 1909, [iv.] 5, 241; Ann. Chim. anal. 1911, 16, 251). According to Spallino (Gazz. 1913, 43, ii, 482) the silicotungstate should be ignited. A polarimetric method has been described by Tingle and Ferguson (Trans. Roy. Soc. Canada, 1916, [iii.] 10, 27), and the estimation of nicotine in the presence of pyridine bases by Surre (Ann. Falsif. 1911, 4, 331). For titration methyl red is a good indicator (Schick and Hatos, Zeit. Nahr. Genussm. 1914, 28, 269).

Properties. Pungent, colourless, hygroscopic liquid, b.p. 247°, which becomes brown and resinous in air owing to oxidation (*cf.* Ciamician and Silber, Ber. 1915, 48, 181). Distils unchanged in a current of hydrogen or steam, but suffers oxidation when distilled in air, $D_4^{20}=1·00925$ (Jephcott, Chem. Soc. Trans. 1919, 104). The density increases to 1·04 on addition of water up to 33 p.c. (*cf.* Hudson, Zeitsch. physikal. Chem. 1904, 47, 113). Lævorotatory $[\alpha]_D^{20}=-168·2°$, salts dextrorotatory. The aqueous solution is strongly alkaline and precipitates solutions of many metallic salts. The salts crystallise with difficulty, but the picrate $B,2C_6H_2(NO_2)_3OH$ forms glancing yellow prisms, m.p. 218°, and is characteristic. Nicotine and its salts are precipitated even in dilute solutions by alkaloidal reagents. Nicotine treated with a drop of formaldehyde solution and then with a drop of nitric acid gives a rose-red colouration.

Reactions and constitution. Nicotine reacts with methyl iodide as a ditertiary base, and on oxidation furnishes β-pyridine derivatives, so that it must contain a pyridine nucleus, with a side chain or a second ring attached in the β-position. Pinner first suggested that this residual portion of the molecule consisted of a N-methylpyrrolidine ring (Ber. 1892, 25, 2816; 1893, 26, 292, 769), and this has received support from the synthesis of nicotine by Pictet and collaborators (*ibid.* 1895, 28, 1911; 1898, 31, 2018; 1900, 33, 2355; 1904, 37, 1225)



Nicotine (Pinner).

G. B.

NICOTINIC ACID *v.* BONE OIL.

NIETZKI'S RULE *v.* COLOUR AND CHEMICAL CONSTITUTION.

NIGELLA SEEDS or **BLACK CUMMIN.** The seeds of *Nigella sativa* (Linn.), a ranunculaceous plant growing on the Mediterranean coasts, and in Egypt, Trans-Caucasia, and India, were found by Reinsch, in 1841, to yield 35·8 p.c. of fat oil, 0·8 p.c. of volatile oil, and only 0·6 p.c. of ash. He gave the name of *nigellin* to a bitter extract resembling turpentine, yet soluble in water as well as in alcohol, though not in ether.

By submitting 25 lbs. of fresh seed to distillation, Fluckiger obtained a nearly colourless essential oil, but in smaller quantity than Reinsch. It has a slight odour, somewhat resembling that of parsley oil, with a magnificent bluish fluorescence, as already remarked by Reinsch. In a column 50 mm. long this oil deviates the ray of polarised light 9·8° to the left. Its sp.gr. is 0·8909. The chief part of it, when heated with calcium chloride in a current of dry carbonic acid, distils at 256°. Its composition corresponds with the formula $2C_{10}H_{16},H_2O$. The residual portion, which is almost entirely devoid of rotatory power, after having been rectified by means of sodium, consists of terpenes $C_{10}H_{16}$. The fat oil, extracted by means of boiling ether from seed grown in Germany, previously finely powdered (necessarily including some essential oil which imparted to the ether its fluorescence), is a fluid fat which does not congeal at 15°: it consists chiefly of olein, together with a considerable amount of a solid fatty acid, probably a mixture of palmitic and myristic acids.

It is stated in the Pharmacopœia of India that nigella seeds are carminative, and they were formerly so regarded in Europe. In the East, generally, they are used as a condiment to food, and in Greece, Turkey, and Egypt they are frequently strewed over the surface of bread and cakes in the same manner as anise or sesame. The fixed oil of the seeds is also expressed for use.

NIGER SEED OIL is obtained from the *achenes* of *Guizotia abyssinica* (Linn.), Cass. (*Guizotia oleifera*, D.C.), a plant indigenous to Abyssinia, and largely cultivated not only in East Africa, but also in the East and West Indies. The *achenes* contain from 40 to 45 p.c. of oil. For the chemical and physical characters of this oil, *see* tables, OILS, FIXED, AND FATS.

Niger seed is crushed in Hull and Marseilles, and of late years the oil has been used to an increased extent as a substitute for linseed oil in soap-making, &c. It yields only a trace of a bromide insoluble in ether, so that its presence in linseed oil reduces the proportion of insoluble bromide given by the latter. J. L.

NIGHT BLUE. A colouring matter obtained by the action of *p*-tolyl - *a* - naphthylamine on tetramethyl-diamino-benzophenone. Resembles Victoria blue. *V.* TRIPHENYLMETHANE COLOURING MATTERS.

NIGRISIN is the commercial name for a basic grey dyestuff formed when aqueous or alcoholic solutions of nitrosodimethylaniline hydrochloride are boiled It forms a black powder soluble in water to a reddish-grey solution which is changed to blue-grey on addition of acid. 1 litre of water at 100° dissolves 80 grams of nigrisin. In sulphuric acid it forms a pure grey solution, which, on addition of water, turns to red- then blue-grey. It is oxidised by nitric acid and reduced by stannous chloride and hydrochloric acid, and by zinc-dust and acid. Potassium dichromate produces a brown precipitate soluble in acetic or tartaric acid with a grey-blue, in hydrochloric acid with a red-blue colour. Nigrisin is distinguished by its purity of shade, strong colouring power, fastness, and the variety of compound shades which it is capable of yielding when mixed with other dyestuffs (Baumann, Bull. Soc. Ind. Mulhouse, 1890, 65).

Nigrisin does not require a mordant for dyeing bleached cotton, and full shades are obtained with 1-3 p.c. of the dye. Cotton mordanted with antimony tannate also takes the dye well; in this case the material is padded in a solution containing 2–10 grams of the dye per litre. It is then dried and steamed, or before drying it may be passed through 0·5 p.c. solution of potassium dichromate at 60°, when an insoluble chromate of the colour-base is formed.

Nigrisin is formed and simultaneously fixed upon the fibre when cotton is printed with the following mixture and then steamed for about 3 minutes: 100 grams of nitrosodimethylaniline hydrochloride, 1 litre of warm water, 1¼ litre of starch paste thickening, 1½ gum tragacanth paste (6 : 100). In the presence of an organic acid a grey (similar to that formed by nigrisin on unmordanted cotton) is produced. If the organic acid is replaced by tannin, and after steaming it is fixed with tartar emetic and washed, a deep rich-grey is obtained. By varying the conditions of dyeing and by the introduction of reducing agents, white and colour discharge effects upon a grey ground are obtained (Federmann, Bull. Soc. Ind. Mulhouse, 1909, 79, 251). The grey colour mixtures can also be made to give blacks (Brandt, J. Soc. Chem. Ind. 1900, 1106).

NIGROSINES *v.* INDULINES.

NIGROTIC ACID *v.* NAPHTHALENE.

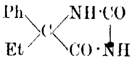
NILE BLUES *v.* OXAZINE COLOURING MATTERS.

NIOBITE *v.* COLUMBITE; also COLUMBIUM.

NIOBIUM *v.* COLUMBIUM.

NIRVANINE is the diethylglycocoll compound of 5-amino-2-hydroxybenzoic methyl ester. It forms a hydrochloride of neutral reaction which produces complete anæsthesia of a longer duration than that caused by cocaïne (Einhorn and Heinz, Pharm. J. 1889, 62, 95), *v* SYNTHETIC DRUGS.

NIRVANOL. $\gamma\gamma$-Phenylethylhydantoin



obtained by the action of potassium cyanate on the hydrochloride of ethyl-α-amino-α-phenylbutyrate. Soluble in 1650 parts of cold and in 110 parts of hot water, in 20 parts of spirit. Has a hypnotic action of about the same intensity as 'luminal' (phenylethylbarbituric acid), but is less toxic. Its hypnotic action is greater than that of veronal (diethylbarbituric acid).

NITON. Sym. Nt. At.wt. and mol.wt. 222·4. The name given by Gray and Ramsay (Proc. Roy. Soc. 1911, A, 84, 536) to the gaseous emanation of radium discovered by Dorn (Naturforsch. Ges. fur Halle a S. 1900). Niton, which has only been obtained in minute quantities, is prepared by heating a compound of radium or by dissolving it in water and pumping off the gases slowly produced. Oxygen, hydrogen, carbon dioxide, and nitrogen are successively removed by means of heated copper, copper oxide, phosphoric pentoxide, fused potassium hydroxide and heated lithium respectively, the niton left is then liquefied at −150° to −170°, and the helium present, together with a little niton, is pumped off (Debierne, Compt. rend. 1909, 148, 1264; Ann. Physique, 1915, [ix.] 3, 18; Rutherford, Phil. Mag. 1908, 16, 300).

From a comparison of the γ-ray activity of the pure product with that of radium in radioactive equilibrium, it is found that the volume of emanation in equilibrium with 1 gram of radium is equal to 0·605 cubic mm. (Debierne).

Niton is a member of the family of inert gases. Its density, measured by means of a microbalance sensitive to 2×10^{-6} mgm. with about $\frac{1}{1400}$ mgm. of material, gave a value of 223 for the molecular weight (Gray and Ramsay, *l.c.*; Compt. rend. 1910, 151, 126), but the value 222·4 is preferred for theoretical reasons. The direct density measurements are confirmed by the effusion experiments of Debierne (Compt. rend. 1910, 150, 1740), and the diffusion experiments of Perkins (Amer. J. Sci. 1908, [iv.] 25, 461), which gave the values 220 and 235 respectively for the molecular weight (for other determinations, *v.* Rutherford and Brooks, Trans. Roy. Soc. Canada, 1901; Curie and Danne, Compt. rend. 1903, 137, 1314; Bumstead and Wheeler, Amer. J. Sci. 1904, [iv.] 17, 97; Makower, Phil. Mag. 1905, [vi.] 9, 56; Chaumont, Le Radium, 1909, 6, 106; Debierne, Ann. Physique, 1915, [ix.] 3, 62). Niton therefore occupies the position in group O of the Periodic Scheme in the same series as, and immediately preceding, radium (*cf.* Gray and Ramsay, Chem. Soc. Trans. 1909, 95, 1073; Rankine, Phil. Mag. 1911, [vi.] 21, 45).

Niton undergoes a rapid diminution in volume to one-half the original amount when it is isolated. The gas, both before and after this change, obeys Boyle's Law. Niton is condensed to a solid at the temperature of liquid air. Both liquid and solid niton are phosphorescent. The critical temperature is 104·5°, the critical pressure 62·5 atmos., and the boiling-point is −62° (Rutherford and Soddy, Phil. Mag. 1903, [iv.] 5, 561; Rutherford, *ibid.* 1909, [vi.] 17, 723; Gray and Ramsay, Chem. Soc. Trans. 1909, 95, 1073; Laborde, Compt. rend. 1909, 148, 1591). Niton possesses a definite spectrum (Ramsay and Collie, Proc. Roy. Soc. 1904, 73, 470; 1908, 81, A, 210: Rutherford and Royds, Phil. Mag. 1908, [vi.] 16, 313; Royds, *ibid.* 1909, [vi.] 17, 202; Proc. Roy. Soc. 1908, [vi.] 82, 22; Watson, *ibid.* 1909, A, 83, 50; Debierne, *l.c.*)

In the presence of niton, slow decomposition of water, ammonia, hydrogen chloride, and the oxides of carbon occurs (Ramsay, Chem. Soc. Trans. 1907, 91, 931; Cameron and Ramsay, *ibid.* 1907, 91, 1593; 1908, 93, 966, 992; Perman, *ibid.* 1908, 93, 1775; Usher, *ibid.* 1910, 97, 389; Rutherford and Royds, Phil. Mag. 1908, [vi.] 16, 812; Curie and Gleditsch, Compt. rend. 1908, 147, 345). On the other hand, it is capable of producing chemical combination, as, for example, the union of electrolytic oxygen and hydrogen. For the colouring and thermoluminescence of glass produced by radium emanation, *see* Lind, J. Phys. Chem. 1920, 24, 437. Niton spontaneously decomposes, producing helium and other substances. For radioactive properties of niton, *v.* Radioactivity.

For the disintegration constant and decay of radium emanation ($0·1819\ \text{day}^{-1}=2·106\times10^{-6}\ \text{sec}^{-1}$), *see* Bothe and Lechner (Zeitsch. physikal. Chem. 1921, 5, 335). These values are above 1 p.c. greater than the Curie-Rutherford values

Its amount in the atmosphere would appear to vary with meteorological conditions, the mean emanation content being about 131×10^{-18} curie per c.c. (Olujać, Jahr. Radioaktiv. Elektronik. 1918, 15, 158). Higher values have been found by Zlatarovic (Chem. Zentr. 1920, iii. 334), in the air at Innsbruck, viz. 433×10^{-18} curie per c.c. (extreme values 1110 and 40). Dependence on meteorological factors could only be so far recognised in that rainy periods correspond with lower emanation values.

Ramsay has described an apparatus for 'drawing off' niton, for use as a therapeutic agent, from a radium salt (Lancet, 1914, 186, 1481).

NITRAL. Trade name for purified moist nitrous oxide used as a bactericide under pressure (Bart, Arch. Hyg. 1922, 91, 1).

NITRATINE, *Soda-nitre*, or *Chile saltpetre* (Span. *Salitre sodico*). Sodium nitrate ($NaNO_3$), crystallised in the rhombohedral system) is by far the most abundant of the few naturally-occurring mineral nitrates. It is, however, found only as granular masses and encrustations, although well-formed crystals are readily obtained artificially. These have the form of simple rhombohedra, which in many of their physical characters present a striking resemblance to crystals of calcite. The angles between the faces and also between the perfect rhombohedral cleavages are 73° 30′ (in calcite 74° 55′).[1] The strength of the double refraction is even higher than for calcite, the values of the refractive indices for sodium-light being $\omega=1·5374$, $\epsilon=1·3361$, $\omega-\epsilon=0·2013$ (the corresponding values for calcite being $\omega=1·6585$, $\epsilon=1·4862$, $\omega-\epsilon=0·1723$). On this account attempts have been made to utilise sodium nitrate for the construction of polarising (nicol) prisms to replace the increasingly rare and expensive Iceland-spar, but it is impossible to obtain large crystals sufficiently clear and free from enclosures of the mother-liquid. Sp.gr. 2·27.

In the provinces of Tarapaca and Antofagasta, in northern Chile, the nitrate deposits occur along a narrow belt of country where the westwardly sloping pampas abut against the coast range at an altitude of about 3000 feet. This district extends from the town of Tarapaca in the north to that of Taltal in the south—a distance of nearly 400 miles—and embraces an area of over 8000 square miles. The salt bed has a thickness of 1 to 6 feet and is overlain by 2 to 20 feet of gypsum, clay, sand, and gravel. The crude salt, called 'caliche,' is granular in texture and more or less cavernous; its colour is white, violet, bright yellow, or brown. It consists of from 20 to 60 p.c. of sodium nitrate, together with much sodium chloride and sulphate, and smaller amounts of soluble calcium and magnesium salts, potassium perchlorate, iodides, iodates, borates, &c. In the purification of the salts by re-crystallisation, iodine is a valuable by-product. Chile saltpetre is largely used as a fertiliser, and for the preparation of potassium nitrate and nitric acid, used for the manufacture of explosives &c The quantity annually exported is about two million tons, valued at about £9 per ton.

Extensive deposits of nitratine in association with borates are also reported to occur in southern California, extending over a region from the Mohave Desert in San Bernardino Co. to Death Valley in Inyo Co. The beds are said to be 3–10 feet in thickness, and to contain 15–40 p.c. of sodium nitrate. The so-called 'tafle,' found in the neighbourhood of Maalla and Esneh, on the Nile in Upper Egypt, is a clay or shale of Cretaceous age, impregnated with 13–18 p.c. of sodium nitrate and about the same amount of sodium chloride. It has been used, probably since early times, as a fertilising agent. Similar deposits are also found near Salah in the Sahara.

References.—G. P. Merrill, The Non-Metallic Minerals, 2nd ed. New York, 1910; B. Dammer and O. Tietze, Die Nutzbaren Mineralien, Stuttgart, 1913, i. 363–384; Estadística Minera de Chile en 1906 i 1907, Santiago de Chile, 1909, vol. iii.; H. S. Gale, Nitrate Deposits, Bull. U. S. Geol. Survey, 1912, No. 523. For references to the literature, *v.* F. W. Clarke, Data of Geochemistry (Bull. U. S. Geol. Survey, No. 616), 1916, *v.* Sodium.

L. J. S

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[1] The term 'cubic nitre' is thus inaccurate and misleading. A rhombohedron of this angle is readily distinguishable from a cuboidal form; and further, the dimorphous potassium nitrate exists as a rhombohedral modification in addition to the more stable orthorhombic modification of prismatic habit. The corresponding orthorhombic modification is not known in sodium nitrate.

NITRATED OILS *v.* Oils, Fixed, and Fats

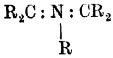
NITRATION. The operation of introducing a nitro group, NO_2, into a nucleus.

NITRE or **SALTPETRE.** Naturally-occurring potassium nitrate, KNO_3, crystallised in the orthorhombic system; sp.gr. 2·11. The less stable rhombohedral modification (sp.gr. 2·27), isomorphous with nitratine, is not known as a mineral. These two modifications of potassium nitrate show remarkably close crystallographic relations to the dimorphous forms of calcium carbonate—calcite and aragonite. As a mineral, nitre shows no very distinctive characters, and it is never found as well-formed crystals. Although of wide distribution, it occurs somewhat sparingly as an efflorescence, consisting of delicate hairs aggregated in silky tufts. It is always of recent formation, and results from the bacterial decay of nitrogenous organic matter of vegetable, or more often animal, origin. The efflorescences are often found on rock surfaces (hence the name saltpetre,[1] from the Latin *sal*, salt, and *petra*, rock), usually in caves and under ledges where protected from the weather. Although sometimes found associated with rocks rich in potassium (*e.g.* in the leucite rocks of the Leucite Hills in Wyoming), the reverse is more often the case. In fact, it is more usually found in limestone caves, *e.g.* in the Mammoth Cave in Kentucky. In dry climates it exudes from the soil; and in India it is systematically collected by the natives. mainly around the villages in the Behar district in Bengal. Here it is formed indirectly by human agencies: urine mainly supplies the nitrogen, and wood-ashes from domestic fires the potassium. About 20,000 tons of partially refined nitre are exported annually from India.

References.—H. S. Gale, Nitrate Deposits, Bull. U. S. Geol. Survey, 1912, No. 523; Nitrates (1913–1919), Imp. Min. Res. Bur London, 1920 *V.* Potassium. L. J. S

NITRE, CUBIC, *v.* Sodium and Nitratine.

NITRENES. Compounds of the type



$$\begin{array}{l}R_2C:N:CR_2\\ \,|\\ R\end{array}$$

comparable with the allenes $R_2C:C:CR_2$ (*cf.* Staudinger and Miescher, Helv. Chim. Acta, 1919, 2, 554).

NITRIC ACID, MANUFACTURE OF. See art. Nitrogen.

NITRIFICATION *v.* Soils.

NITRILES. Prussic acid, being tautomeric in character, gives rise to two classes of esters, the *normal cyanides* or *nitriles* and the iso*cyanides*, iso*nitriles* or *carbylamines*.

The **nitriles** all contain the $-C{\equiv}N$ group, and they can be regarded either as hydrocarbons with one hydrogen atom replaced by the CN group, or as acids in which the COOH group has been converted into the CN group; *e.g.* CH_3CN is known either as methyl cyanide or as acetonitrile. The nitriles were discovered in 1834 by Pelouze, who obtained propionitrile by distilling barium ethyl sulphate with potassium cyanide.

Methods of preparation.—(a) *Aliphatic nitriles.*

(1) By heating alkyl halides (preferably iodide) with potassium cyanide in alcoholic solution at 100°.

(2) By distilling the salts of alkyl-sulphuric acids with potassium cyanide. (In each of these methods a little *iso*cyanide is also produced.)

(3) By heating alkyl *iso*cyanides to 250°.

(4) By treating cyanogen chloride with zinc alkyl. (In the above four methods the carbon chain is lengthened.)

(5) By the dry distillation of the acid amide or of the ammonium salt of the acids with phosphorus pentoxide or other dehydrating agent.

(6) By passing the acids together with a stream of ammonia through a red-hot tube.

(7) By converting the aldehydes into aldoximes, which are then dehydrated by acetic anhydride.

(8) By treating primary amines containing more than five carbon atoms with potassium hydroxide and bromine.

(b) *Aromatic nitriles.* By methods 3, 5, and 7.

(4) By diazotising a primary aromatic amine and decomposing the diazo- chloride thus formed with cuprous cyanide or with potassium cyanide and copper sulphate.

(5) By the action of potassium hydroxide and bromine on the primary arylalkylamines.

(6) By distilling the acids with potassium or lead thiocyanate. According to Reid (Amer. Chem. Journ. 1910, 43, 162) this method serves well for the preparation of aliphatic nitriles if the lead thiocyanate be mixed with the lead or zinc salt of the fatty acid, or if instead of lead thiocyanate, a mixture of lead ferrocyanide and sulphur be used.

(7) By replacing the hydrogen atoms of the hydrocarbons directly with $-CN$ by passing cyanogen into the boiling hydrocarbon mixed with aluminium chloride.

(8) By desulphurising the mustard oils with metallic copper.

(9) By heating the diarylthioureas with zinc-dust.

(10) By distilling the formanilides with strong hydrochloric acid or with zinc-dust.

(11) By distilling the alkali benzene sulphonates with potassium cyanide or with potassium ferrocyanide.

Properties (*aliphatic* and *aromatic*).—The nitriles are colourless volatile oils of weakly basic character which have an ethereal odour, are not very soluble in water, and distil unchanged. They possess toxic properties. They are easily hydrolised by acids or alkalis into ammonia and the corresponding acid, the temperature required to effect this change being higher in the aromatic than in the aliphatic series. If an alcoholic solution of hydrochloric or sulphuric acid is used to carry out the hydrolysis, the ester is produced. In this case the triple link between carbon and nitrogen is completely destroyed, but there are many instances in which the nitriles behave as unsaturated compounds, the reactions being additive. Thus nitriles, when heated with water at 180°, or when treated with alkaline hydrogen peroxide at 40°, combine with a molecule of water to form acid amides Similarly with acids they form diacylamines; with acid anhydrides, triacylamines; with sulphuretted hydrogen, thioamides; with hydroxylamine, amidoximes; with nascent hydrogen, amines (Mendius Reaction); with hydrochloric acid, imino-chlorides or imino-ethers, depending on the use of aqueous or alcoholic solutions. The Grignard reagent forms additive compounds with nitriles, and from these, by the action of dilute acids, ketones may be obtained (Blaise, Comp. rend. 1901, 133, 1217)

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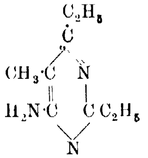
[1] The name nitre is derived from the ancient νίτρον, soda (*v.* Natron).

$$\mathrm{R{\cdot}CN+R'MgX}=\begin{matrix}\mathrm{R}\\\mathrm{R'}\end{matrix}{>}\mathrm{C:NMgX}$$

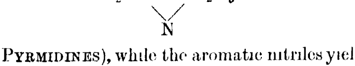
$$\begin{matrix}\mathrm{R}\\\mathrm{R'}\end{matrix}{>}\mathrm{C:NMgX+2H_2O}$$

$$=\begin{matrix}\mathrm{R}\\\mathrm{R'}\end{matrix}{>}\mathrm{CO+NH_3+Mg(OH)X}$$

In common with other unsaturated compounds, the nitriles form polymerisation products. By treatment with sodium (or sodamide) in ether, bimolecular indifferent substances are produced: thus acetonitrile yields the imino-nitrile of acetoacetic acid $\begin{array}{l}\mathrm{CH_3{\cdot}C{=}NH}\\\quad|\\\mathrm{CH_2{\cdot}CN}\end{array}$. On treatment with sodium in the absence of any solvent, trimolecular compounds are produced; in the case of the aliphatic series these are strongly basic substances, amino-pyrimidines, propionitrile yielding amino-methyl-diethyl-pyrimidine



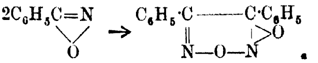
(*v.* PYRMIDINES), while the aromatic nitriles yield cyanuric compounds containing the tricyanogen ring. From dicarboxylic acids two nitriles can be produced, the half-nitrile or nitrilic acid and the dinitrile, *e.g.* oxalic acid yields the dinitrile, oxalonitrile, which is dicyanogen, and the half-nitrile, oxalonitrilic acid, which is cyanoformic acid, and is known only in the form of esters. Similarly phthalic acid, yields the dinitrile, phthalonitrile and the half-nitrile *o*-cyanobenzoic acid, which on heating changes into phthalimide (*v.* PHTHALIC ACID). For individual aliphatic nitriles, *v.* arts. METHYL, ETHYL, &c., and acids from which they are derived. A series of compounds known as nitrile oxides, and formulated as $\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{R{\cdot}C{=}N}}$ has been obtained (Scholl, Ber. 1901, 34, 865; Wieland and Semper, Annalen, 1907, 358, 36), and in the trimolecular form are produced by the spontaneous decomposition in solution of the alkali salts of nitrolic acids



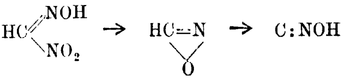
$$\mathrm{3R{\cdot}C(:NOH){\cdot}NO_2=3HNO_2}+\left[\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{R{\cdot}C{=}N}}\right]_3$$

Benzonitrile oxide is readily obtained by the elimination of hydrochloric acid from benzhydroximic chloride $\mathrm{C_6H_5C(:NOH){\cdot}Cl}$.

As a class the nitrile oxides readily polymerise to furoxans, thus benzonitrile oxide is transformed into diphenyl furoxan



whilst on the other hand the formonitrile oxide which should result from methyl nitrolic acid is converted into fulminic acid



Benzonitrile, *Phenyl cyanide*, $\mathrm{C_6H_5{\cdot}CN}$ occurs in coal tar oil (Kramer and Spilker, Ber. 1890, 23, 83). It may be prepared by the prolonged heating of phenyl *iso*cyanide at 200°–220° (Weith, Ber. 1873, 6, 213); by the dry distillation of ammonium benzoate (Fehling, Annalen, 49, 91); or by distilling the aqueous solution with baryta (Laurent and Gerhardt, J. 1849, 327; Wohler, Annalen, 192, 362), lime (Anschutz and Schultz, *ibid.* 196, 48), phosphorus pentoxide (Buckton and Hofmann, *ibid.* 100, 115), phosphorus pentachloride (Henke, *ibid.* 106, 276), or phosphorus pentasulphide (Henry, Ber. 1869, 2, 307); by distilling benzaldoxime with acetic anhydride (Lach, *ibid.* 1884, 17, 471); by diazotising aniline, and decomposing the diazobenzene chloride thus formed with potassium cyanide and copper sulphate (Sandmeyer, *ibid.* 2563); by distilling benzoic acid with potassium thiocyanate (Letts, *ibid.* 1872, 5, 673); by passing cyanogen into boiling benzene in the presence of aluminium chloride (Desgrez, Bull. Soc. chim. [iii.] 13, 735); by heating benzene and cyanogen chloride or bromide in the presence of aluminium chloride (Friedel and Crafts, Ann. Chim. Phys [vi.] 1, 528; Merz and Weith, Ber. 1877, 10, 756); by the interaction of potassium fulminate and benzene in the presence of aluminium chloride (Scholl, Ber. 1899, 32, 3496); by treating potassium benzoate with cyanogen bromide (Cahours, Annalen, 108, 319); by desulphurising phenyl mustard oil with metallic copper (Weith, Ber. 1873, 6, 213); by distilling formanilide in a stream of hydrogen over heated zinc (Gasiorowski and Merz, *ibid.* 1885, 18, 1002); by heating potassium benzene sulphonate (Merz, Zeitsch. Chem. 1868, 33), or triphenylphosphate (Scrughan, Annalen, 92, 318; Heim, Ber. 1883, 16, 1771) with potassium cyanide; by treating benzamide, potassium cyanate or thiocyanate with benzoyl chloride (Limpricht, Annalen, 99, 117; Schiff, *ibid.* 101, 33); by heating chloro- or bromobenzene with potassium ferrocyanide at 400° (Merz and Weith, Ber. 1875, 8, 918; 1877, 10, 749); by heating iodobenzene and silver cyanide at 300° (Merz and Schelnberger, Ber. 1875, 8, 1630); by treating a mixture of bromobenzene and cyanogen chloride in ethereal solution with sodium (Klason, J. pr. Chem. [ii.] 35, 83); by the interaction of ethylene dicyanide and benzoic acid (Matthews, J. Amer. Chem. Soc. 1898, 20, 650); by heating hippuric acid either alone or better with anhydrous zinc chloride at 240° (Limpricht and Uslar, Annalen, 88, 133; Gossmann, *ibid.* 100, 74); by passing dimethylaniline through a heated tube (Nietzki, Ber. 1877, 10, 474); and by the interaction of magnesium nitride and benzoic anhydride (Emmerling, *ibid.* 1896, 29, 1635).

Benzonitrile is a colourless oil, having an odour resembling that of benzaldehyde, b.p. 190·7° (corr.), sp.gr. 1·0101 at 15°/15° (Perkin, Chem. Soc. Trans. 1896, 1244; Kopp, Annalen, 98, 373), m.p. −12·9° (Schneider, Zeitsch.

physikal. Chem. 19, 157); soluble in alcohol and ether, and in 100 parts of boiling water. On boiling benzonitrile with potassium hydroxide it is hydrolysed to benzoic acid and ammonia, while by digesting it for many hours with dilute potassium hydroxide at 40°, benzamide is produced (Rabaut, Bull. Soc. chim. [iii.] 21, 1075). Benzylamine is formed by reduction with alcoholic hydrochloric acid and zinc (Mendius, Annalen, 121, 144). According to Sabatier and Senderens (Compt. rend. 1905, 140, 482), hydrogenation in the presence of reduced nickel at 200° yields toluene and ammonia; but Frebault (*ibid.* 1036) states that by embedding the nickel in iron filings to ensure an even temperature, at 250° the products are benzylamine, dibenzylamine and possibly a trace of tribenzylamine. Chlorine in the presence of sunlight yields benzonitrile hexachloride (Mathews, Chem. Soc. Trans. 1900, 1273). Forms compounds with antimony haloids and other metallic salts.

Benzonitrile oxide, *v.* Wieland, Ber. 1907, 40, 1667; Werner and Buss, Ber. 1894, 27, 2193. Addition compounds with platinous chloride, *v.* Hofmann and Bugge, *ibid.* 1907, 40, 1772; Ramberg, *ibid.* 2578.

The *iso***cyanides** contain the group $-N{=}C$ (Nef, Annalen, 1892, 270, 267; 1895, 287, 265) They were first prepared in 1866 by Gautier by treating alkyl iodides with silver cyanide. Later Hofmann obtained them by the interaction of potassium hydroxide, chloroform and primary amines. They are also formed in small quantity in some of the methods for preparing the nitriles (*v. supra*).

The *iso*cyanides are colourless, volatile liquids, having a most disagreeable odour, and are readily soluble in alcohol and ether, sparingly so in water. Though the *iso*cyanides are not basic, yet they combine with hydrochloric acid in ethereal solution to form compounds of the type $2R{\cdot}NC,3HCl$, but these substances are unstable to water. The *iso*cyanides are more easily hydrolysed than the nitriles, dilute acids or water at 180° effecting this, the products being formic acid and primary amines. They are stable to alkalis. Glacial acetic acid converts them into alkylformamides by the addition of one molecule of water. On reduction there are formed secondary amines, one of the groups being methyl. As a class they are characterised by the formation of addition compounds; thus, when heated with sulphur at 130°C. they yield mustard oils; with hydrogen sulphide at 100°C., alkyl thioformamides; with acid chlorides the amide-chlorides of ketonic acids. On oxidation with mercuric oxide, *iso*cyanic esters are produced. On the constitution of the *iso*nitriles, *see* Nef (Annalen, 1892, 270, 260; 1894, 280, 291; 1899, 309, 154).

Alkyl *iso*cyanides *v.* arts. METHYL, ETHYL, &c.

Phenyl *iso*cyanide, *Phenylcarbylamine*

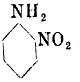
$$C_6H_5{\cdot}N{=}C$$

may be prepared by the interaction of aniline, chloroform, and potassium hydroxide in alcoholic solution at 50° (Hofmann, Annalen, 144, 117; Nef, *ibid.* 270, 274); or by the action of chloroform and dry powdered caustic alkali on aniline in the absence of any solvent (Biddle and Goldberg, *ibid.* 310, 7); by the action of chloroform, carbon tetrachloride, hexachlorethane, bromoform, iodoform, or chloral on phenyl hydrazine in the cold (Brünner and Vuilleumier, Chem. Zentr. 1908, ii. 588).

Phenyl *iso*cyanide, when freshly prepared, is a green liquid; after a few minutes it changes to a pale blue, then to a dark blue liquid, and finally, after some months to a brown resin, b.p. 165° (with decomposition), sp.gr. 0·9775 at 15°/15°. By passing dry hydrogen chloride into a dry ethereal solution of phenyl *iso*cyanide the hydrochloride $2C_6H_5{\cdot}NC,3HCl$ is formed; this is decomposed by water (Nef. Annalen, 270, 303). By passing chlorine into the dry ethereal solution a chloride is obtained; this chloride can also be prepared by passing chlorine into phenyl mustard oil (Nef, *ibid.* 282), and on treatment with water at 100°, *sym*-diphenylurea, carbon dioxide, hydrochloric acid, and aniline are the products. Bromide, *v.* Lengfield and Stieglitz, Amer. Chem. J. 17, 101. Phenyl *iso*cyanide is readily hydrolysed by dilute acids into aniline and formic acid. Glacial acetic acid converts it into formanilide, and a trace of acetanilide; thioacetic acid yields acetanilide (Pawlewski, Ber 1899, 32, 1425). It combines with sulphur, yielding phenyl mustard oil (Weith, *ibid.* 1873, 6, 210); with sulphuretted hydrogen it yields thioformanilide. By heating phenyl *iso*cyanide at 200°–220°, benzonitrile is produced (Weith, *ibid.* 213). Addition compounds with platinous chloride, *v.* Hofmann and Bugge, Ber. 1907, 40, 1772; Ramberg, *ibid.* 2578.

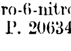
***β*-NITROANILINE RED** *v.* AZO- COLOURING MATTERS.

NITROANILINES. By the direct nitration of aniline, a mixture of *o*-, *m*-, and *p*-nitroanilines is produced. Aniline is dissolved in 6 to 8 times the calculated quantity of nitric acid, mixed with an equal volume of sulphuric acid, the temperature being kept below 0°. The liquid is poured on to ice, and diluted with ice-water until *o*-nitroaniline ceases to be precipitated. After filtration, the liquid is neutralised with sodium carbonate, and the *m*- and *p*-nitroanilines separated by fractional precipitation, *p*-nitroaniline being first precipitated as a yellowish-brown powder, and then the *m*- compound, which is pure yellow (Nietzki and Benckiser, Ber. 1885, 18, 295; Pinnow and Müller, *ibid.* 1889, 24, 150; Bruns, *ibid.* 1895, 28, 1954). According to Holleman, Hartogs and van der Linden (Ber. 1911, 44, 704), in the direct nitration of aniline the product consists mainly of the *p*- compound, with small quantities of the *o*- compound, modified by the presence of aniline sulphate, which leads to the formation of the *m*- product, and of the intermediate formation of phenylnitroamine, which gives rise to *o*-nitroaniline. For an examination of Holleman's method of estimating the relative proportion of the three isomerides in a mixture, *see* Nichols, J. Amer. Chem. Soc. 1918, 40, 400.

o-**Nitroaniline**  may be prepared by the reduction of *o*-dinitrobenzene with ammonium sulphide (Körner, Gazz. chim. ital. 4, 305; *cf.* Rinne and Zincke, Ber. 1874, 7, 1374); by heating *o*-dinitrobenzene (Laubenheimer, *ibid.*

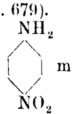
1878, 11, 1155; de Bruyn, Rec. trav. chim. 13, 121), *o*-nitrophenol (Merz and Ris, Ber. 1886, 19, 1751), *o*-nitroanisole (Salkowski, Annalen, 174, 278), or *o*-bromonitrobenzene (Walter and Zincke, Ber. 1872, 5, 114) with alcoholic ammonia; by heating *o*-nitrobenzanilide with dilute sodium hydroxide (Hübner, Annalen, 208, 278; Lellmann, *ibid.* 221, 6); by treating an aqueous solution of *o*-phenylenediamine with sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3084); by treating oxanilide with strong sulphuric acid, nitrating the oxanilidedisulphonic acid thus formed, and decomposing the dinitro-oxanilidedisulphonic acid by boiling with water (Wulfing, D. R. PP. 65212, 66060; Frdl. iii. 44, 45). It is manufactured by gradually adding 40 kilos. of acetanilide to 80 kilos. of sulphuric acid (66°Bé.) with constant stirring, and keeping the temperature below 50°. A mixture of 36 kilos. of nitric acid (36°–37°Bé.) and 40 kilos. of sulphuric acid (66°Bé.) is then run in, the temperature being kept between 40° and 50°. Next day the liquid is poured into 200 litres of hot water, *o*- and *p*-nitroacetanilide being precipitated. The nitroacetanilides are deacetylated by heating an aqueous suspension with steam until complete solution occurs; the liquid is cooled to 50° and then poured on ice, *o*-nitroaniline being precipitated. The *n*- compound is obtained by adding 180 kilos. of soda lye (36°Bé.) to the mother liquors and cooling with ice; yield 25 p.c. ortho- and 60 p.c. para- (Pokorný, Bull. Soc. Ind. Mulhouse, 1894, 280; Turner, Ber. 1892, 25, 985; Meldola, Chem. Soc. Trans. 1883, 427; Körner, Gazz. chim. ital. 4, 305).

o-Nitroaniline crystallises in orange-yellow needles, m.p. 71·5°; 1 litre of water dissolves 1·256 grams at 25°; dielectric constant (*v.* Löwenherz, Zeitsch physikal. Chem. 25, 407). Electrolytic reduction in sodium carbonate solution yields *o*-phenylenediamine (Rohde, Zeitsch. Elektrochem. 7, 339); this can be also effected by boiling with zinc and water. By boiling with ethyl chlorocarbonate, *o*-nitrophenylurethane is produced (Rudolph, Ber. 1889, 12, 1295), and with phthalic chloride *o*-nitrophthalanil is the product (Pawlewski, *ibid.* 1895, 28, 118). 3-chloro-6-nitroaniline (*v.* Bad. Anil. Soda Fab. D. R. P. 206345; Chem. Soc. Abstr. 1909, i. 297).



***m*-Nitroaniline** may be prepared by the reduction of *m*-dinitrobenzene with ammonium or sodium sulphide (Muspratt and Hofmann, Annalen, 57, 215; Körner, Gazz. chim. ital. 4, 305; Beilstein and Kurbatow, Annalen, 176, 44; Cobenzl, Chem. Zeit. 1913, 37, 299) (for details, *see* Cain's Manufacture of Intermediate Products for Dyestuffs) with stannous chloride (Anschütz and Heusler, Ber. 1886, 19, 2161), or with iron and sulphuric or hydrochloric acids (Wülfing, D. R. P. 67018; Frdl. iii. 47); by treating *m*-nitrobenzanilide with dilute alkalis (Hübner, Annalen, 208, 278); by treating an aqueous solution of *m*-phenylenediamine with sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3084); or by adding aniline nitrate to sulphuric acid at low temperature (Levinstein, D. R. P. 30889).

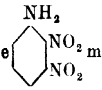
m-Nitroaniline crystallises in large yellow needles, m.p. 112·4° (Hübner, Annalen, 208, 298), b.p. 285°, sp.gr. 1·430 (Schröder, Ber. 1879, 12, 563). Soluble in hot water and the usual organic solvents (Carnelley and Thomson, Chem. Soc. Trans. 1883, 786). Electrolytic reduction in alkaline solution yields *m*-azoaniline (Elbs and Kopp, Zeitsch. Elektrochem. 1895, 5, 108; Wulfing, D. R. P. 108427; Chem. Zentr. 1900, i. 1175); reduction with sodium stannite in alkaline solution yields di*meta*diaminoazoxybenzene (Meldola, Chem. Soc. Trans. 1896, 7), and in hot alkaline solution *m*-azoxyaniline is formed (Poirrier and Rosenstiehl, D. R. P. 44045; Frdl. ii. 436). By boiling with phthalic chloride, *m*-nitrophthalanil is produced (Dobreff, Ber. 1895, 28, 939; Pawlewski, *ibid.* 1894, 27, 430; 1895, 28, 1118). For methylation, *v.* Staedel and Bauer, *ibid.* 1886, 19, 1939; chlorination, *v.* Körner and Contardi, Atti R. Accad. Lincei. 1909, [v.] 18, i. 93; bromination, *ibid.* 1908, [v.] 17, i. 465; iodination, *ibid.* ii. 679).



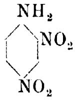
***p*-Nitroaniline** may be prepared by heating *p*-nitrophenol (Merz and Ris, Ber. 1886, 19, 1753), or *p*-chloronitrobenzene (Engelhardt and Latschinow, Zeitsch. Chem. 1870, 232; Clayton Aniline Co., D. R. P. 148749; Chem. Soc. Abstr. 1904, i. 393) with strong aqueous ammonia; by boiling *p*-nitrobenzanilide with dilute potassium hydroxide (Hubner, Annalen, 208, 278); by oxidising *p*-nitrosoaniline (O. Fischer, *ibid.* 286, 154); by treating an aqueous solution of *p*-phenylenediamine with sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3084); by nitrating benzylidineaniline with equal quantities of sulphuric and nitric acids, and dissolving out the product with water (Bayer and Co., D. R. P. 72173; Frdl. iii. 48); and by nitrating acetanilide (*v. o-Nitroaniline*) (*cf.* Muller, Chem. Zeit. 1912, 36, 1055).

p-Nitroaniline crystallises in long yellow needles, m.p. 148·3°; sp.gr. 1·424 (Schröder, Ber. 1879, 12, 563); readily soluble in hot water and the usual organic solvents (Carnelley and Thomson, Chem. Soc. Trans. 1883, 786). Electrolytic reduction in the presence of sulphuric acid yields *p*-diaminobenzene sulphate (Noyes and Dorrance, Ber. 1895, 28, 2349), but in the presence of sodium carbonate *p*-phenylenediamine is the product (Rohde, Zeitsch. Elektrochem. 7, 339). *p*-Phenylenediamine is also formed by reduction with zinc and water, by treatment with hydrogen in presence of finely divided nickel, or with hyposulphurous acid (Goldberger, Oester, Chem. Zeit. 3, 470). By heating with ethyl chlorocarbonate, *p*-nitrophenylurethane is formed (Hager, Ber. 1884, 17, 2625); and with phthalic chloride *p*-nitrophthalanil (Dobreff, *ibid.* 1895, 28, 939; Pawlewski, *ibid.* 1894, 27, 3430; 1895, 28, 1118).

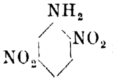
For chlorination, *v.* Flürscheim, Chem. Soc. Trans. 1908, 1772; oxidation with hypochlorites, *v.* Bayer & Co., D. R. P. 83525; Frdl. iv. 1017; AZO- derivatives of the nitroanilines, *v.* AZO-COLOURING MATTERS; constitution of the nitroanilines, *v* Hirsch, Ber. 1903, 36, 1898; absorption spectrum, *v.* Baly, Edwards and Stewart, Chem. Soc. Trans. 1906, 514; mercury salts, *v.* Jackson and Peakes, Amer. Chem. J. 1908, 39, 567; condensation products with chloral, *v.* Wheeler and Weller, J. Amer. Chem. Soc. 1902, 24, 1063.

2 : 3-Dinitroaniline 

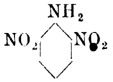
may be prepared by heating 2 : 3-dinitroacetanilide with sulphuric acid (Wender, Gazz. chim. ital. 19, 226); orange-yellow needles, m.p. 127°; soluble in alcohol.

2 : 4-Dinitroaniline 

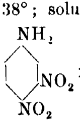
may be prepared by heating 2 : 4-dinitrosuccinanil (Gottlieb, Annalen, 85, 24) or 2 : 4-dinitroacetanilide (Rudnew, Zeitsch. Chem. 1871, 202) with potassium hydroxide; by heating 1-chloro-2 : 4-dinitrobenzene (Engelhardt and Latschinow, *ibid.* 1870, 233), 1-bromo-2 : 4-dinitrobenzene (Clemm, J. pr. Chem. [ii.] 1, 145), 2 : 4-dinitroanisol (Salkowski, Annalen, 174, 263), or 2 : 4-dinitrophenol (Barr, Ber. 1888, 21, 1542) with alcoholic ammonia. Yellow crystals, m.p. 176°; insoluble in water, soluble in alcohol and ether. On reduction with ammonium sulphide, *o*- and *p*-nitrophenylenediamines are produced (Kehrmann, Ber. 1895, 28, 1707); by boiling with alcoholic potassium cyanide, 2 : 4-dinitroaminophenol is formed (Lippmann and Fleissner, Monatsh. 7, 95), and with potassium hydroxide, 2 : 4-dinitrophenol (Willgerodt, Ber. 1876, 9, 979). For derivatives, *v.* Jaeger, Proc. K. Akad. Wetensch. Amsterdam, 1906, 9, 23.

2 : 5-Dinitroaniline 

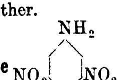
may be prepared by heating 2 : 5-dinitroacetanilide with sulphuric acid (Wender, Gazz. chim. ital. 19, 233); orange-yellow needles, m.p. 137°; readily soluble in alcohol.

2 : 6-Dinitroaniline 

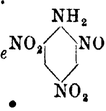
may be prepared by heating 2 : 6-dinitroanisol (Salkowski, Annalen, 174, 273) or 1-iodo-2 : 6-dinitrobenzene (Kröner, J. 1875, 345) with alcoholic ammonia; yellow needles, m.p. 138°; soluble in alcohol.

3 : 4-Dinitroaniline 

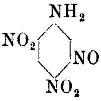
may be prepared by heating 3 : 4-dinitroacetanilide with sulphuric acid (Wender, Gazz. chim. ital. 19, 233); citron-yellow needles, m.p. 154°; soluble in alcohol, almost insoluble in ether.

3 : 5-Dinitroaniline 

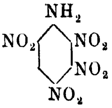
may be prepared by reducing 1 : 3 : 5-trinitrobenzene with ammonium sulphide (Bader, Ber. 1891, 24, 1653); yellow needles, m.p. 159°; soluble in alcohol and ether, almost insoluble in benzene.

2 : 4 : 6-Trinitroaniline, *Picramide* 

may be prepared by heating 1-chloro-2 : 4 : 6-trinitrobenzene with ammonia (Pisani, Annalen, 92, 326) or by nitrating *o*- or *p*-nitroanilines (Witt and Witte, Ber. 1908, 41, 3090); dark yellow needles, m.p. 188°. By reduction with tin and hydrochloric acid 2 : 4 : 6-triaminophenol is formed (Hepp, Annalen, 215, 350; Salkowski, *ibid.* 174, 261). By heating with potassium hydroxide, picric acid is produced (*q.v.*).

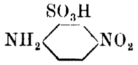
2 : 4 : 5-Trinitroaniline 

is obtained by nitrating *m*-nitroacetanilide (Witt and Witte, *l.c.*), m.p. 183°.

2 : 3 : 4 : 6-Tetranitroaniline 

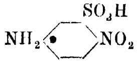
is prepared by nitrating *m*-nitroaniline, 2 : 3- or 2 : 4-dinitroanilines (Flurscheim and Simon, Chem. Soc. Proc. 1910, 81); yellow crystals, m.p. 212°.

4-Nitroaniline-2-sulphonic acid

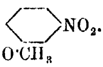


Prepared by heating 2-chloro-5-nitrobenzene sulphonic acid with alcoholic ammonia at 120°–140°, thus forming the ammonium salt (Fischer, Ber. 1891, 24, 3789).

4-Nitroaniline-3-sulphonic acid



Formed by boiling sodium metanilate with acetic acid, dissolving in sulphuric acid, cooling and adding a cooled mixture of nitric acid (sp.gr. 1·385) and sulphuric acid, pouring on to ice and separating the product. Yellow needles, sparingly soluble in cold water and alcohol (Eger, Ber. 1888, 21, 2579).

***o*-NITROANISOLE** 

Obtained by methylating *o*-nitrophenol (Jansen, Chem. Zeitsch. 1913, 12, 171), or by acting on *o*-chloronitrobenzene with sodium hydroxide and methyl alcohol (Brand, J. pr. Chem. 1903, ii. 67, 145).

NITROBENZALDEHYDES *v.* Benzaldehyde.

NITROBENZENE *v.* Benzene.

NITROCALCITE. A mineral consisting of hydrated calcium nitrate, $Ca(NO_3)_2+nH_2O$, probably identical with the artificial monoclinic salt $Ca(NO_3)_2,4H_2O$ (sp.gr. 1·90). It occurs as an efflorescence of white silky fibres, and is usually found in limestone caves in association with nitre (*q.v.*). During the American war of 1812 the earth on the floors of the Mammoth Cave in Kentucky and the Wyandotte Cave in southern Indiana was systematically leached for the manufacture of saltpetre. The mineral is also recorded from Hungary and Spain, and is said to be abundant in caves in Venezuela. It is sometimes seen as an efflorescence on the walls of stables ('wall-saltpetre'). Calcium nitrate is now manufactured on a large scale from atmospheric nitrogen for use as a fertiliser. *V.* CALCIUM. L. J. S.

NITROCELLULOSES *v.* EXPLOSIVES.

NITROCINNAMIC ACID *v.* CINNAMIC ACID.

NITROCRESOL *v.* NITROPHENOLS AND THEIR HOMOLOGUES.

NITRO DYES *v.* AURANTIA; NAPHTHALENE; and PICRIC ACID.

NITROFORM. Tetranitromethane, *v.* ACETYLENE.

NITROGEN. Symbol N. At.wt. 14·008. Nitrogen was discovered in 1772 by Rutherford, Professor of Botany in the University of Edinburgh. He found that when a small animal was allowed to breathe air in a confined space for a time, and the carbon dioxide thereby produced removed by absorption, a gas still remained which was incapable of supporting respiration. Lavoisier first established the individuality of this gas, and clearly demonstrated its existence in the atmosphere. From its incapacity to support life he gave it the name of *azote*; the name nitrogen, denoting that the gas is an essential constituent of nitre, was subsequently given to it by Chaptal.

Occurrence.—Nitrogen is one of the most widely diffused of the elements, and occurs free in the air, of which it constitutes four-fifths by volume, or, more accurately, 78·06 p.c. (Leduc, Compt. rend. 1896, 123, 805). Volcanic gases contain considerable quantities of nitrogen, and the air-bladders of certain fishes, the bone-cavities of many birds, as well as the cavities of plants, all contain the gas in the free state. It occurs in many meteorites. The nebulæ consist, in part, of free nitrogen, and it is contained in the atmosphere of the sun.

Nitrogen, in a state of combination with oxygen, exists in the air as nitric and nitrous acids, and, combined with hydrogen, as ammonia. According to Hayhurst and Pring (Chem. Soc. Trans. 1910, 868) nitrous gases are present in the atmosphere in quantities which vary from time to time, and are usually greater at high than at low altitudes, to the extent of about 1 in 3,000,000. These compounds are consequently present in rain-water. Nitrogen is an essential constituent of animal and vegetable organisms, and is found in many minerals, but chiefly in saltpetre or potassium nitrate, and Chile saltpetre or sodium nitrate.

PREPARATION.—(A) *From the Atmosphere.*

(*a*) By chemical separation of the oxygen with some reagent with which it easily reacts—

(1) By passing air over reduced iron (Brunner; Spencer, Eng. Pat 3752, 1869).

(2) With hydrogen over platinum sponge (Dumoulin).

(3) Over heated copper turnings (Dumas and Boussingault; Welton, Eng. Pat. 2559, 1879; Franke and Finke, Eng. Pat. 10718, 1912; Cyanid-Gesell. D. R. P. 218671, 1912), or better, mixed with ammonia gas (Lupton, Chem. News, 1876, 33, 90), or with hydrogen (Hulett, J. Amer. Chem. Soc. 1906, 27, 1415).

(4) By absorption with alkaline pyrogallol (Liebig, Annalen, 1851, 77, 107).

(5) With copper and aqueous ammonia (Berthelot, Bull. Soc. chim. [ii.] 13, 314).

An apparatus (*see* Fig. 1) for obtaining nitrogen from air on this principle comprises a reservoir, A, containing a mixture of equal volumes of a saturated solution of commercial ammonium carbonate and ammonia of sp.gr. 0·93. The liquid flows from A at a rate controlled by the screw-clamp, D, and encounters a current of air at the branch, C, which should slope as shown. The fall-tube from A must be long enough to give a pressure at C such that the volume of solution carried up is at least equal to that of the accompanying air without danger of the latter backing up into A. The air-liquid mixture is discharged over the glass bell in the top of B and descends through the column of copper clippings in B. The air, now freed from oxygen, is dried and freed from ammonia with dilute sulphuric acid. The air current serves to ensure the continuous circulation of the liquid through the apparatus (Van Brunt, J. Amer. Chem. Soc. 1914, 36, 1448; J. Soc. Chem. Ind. 1914, 33, 788).

A modified form of this apparatus using solution of ammonia saturated with ammonium chloride has been described by Badger (J. Ind. Eng. Chem. 1919, 11, 1052; Analyst, 1920, 32).

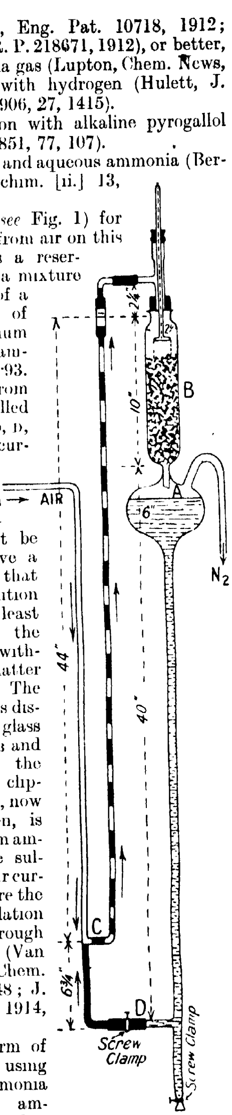


FIG. 1.

(6) With manganous and ferrous hydroxides (Flight, Chem. News, 1882, 45, 105).

(7) With phosphorus.

In these cases, after removal of carbon dioxide and water vapour, the gas obtained is at the most 99 p.c. pure, as the inert gases are still present.

Amongst the many patents for the production of nitrogen on this principle are those of Frank and Caro (nitrogen from combustion gases, *e.g.*

from gas producers, D. R. P. 204882, May 22; 1907).: Eng. Pat. 16963, 1908; Lance and Elworthy, Eng. Pat. 4409, 1906; Riedel, Eng. Pat. 20631, 1909; Braun, Eng. Pat. 22531, 1911; Harger, Eng. Pats. 28075, 1911; 16855, 1912; Cyanide Ges. m.b H. (D R. P. 218671, Nov. 25, 1908; from air passed over copper in specially designed apparatus), Kassner (D. R. PP. 233383, and 234849, May 29, 1910, by absorbing the oxygen with calcium plumbate, alkali manganate, &c.); and Acker (Nitrogen Co. New York, Eng. Pat. 24413, 1910).

The American Cyanamide Co. uses a 'copper' process for the production of nitrogen, the reduction being effected by coke-oven gas in connection with carbide manufacture. A temperature of 450° is employed, giving an output of 200 cub. ft. per hour (Bucher, J. Ind. Eng Chem. 9, 1917, 233.

(β) By fractional distillation of liquid air. The bulk of the uncondensed gas is nitrogen, and the vapour boiling off from the liquid is mainly the more volatile nitrogen, the liquid after standing in a Dewar flask for some time being practically pure oxygen (v. Stock and Nielson, Ber. 1906, 39, 3393). Nitrogen thus obtained always contains argon to the extent of about 0·5 p.c.

For the distillation of mixtures of liquid nitrogen and oxygen, v. Baly (Phil. Mag. 1900, [v.] 49, 517), Inglis and Coates (Chem. Soc. Trans. 1906, 886), Inglis (Phil. Mag. 1906, [vi.] 11, 640).

Erdmann (Ber. 1906, 39, 1207) describes a commercial method for condensing large quantities of nitrogen, in practically pure condition.

Many forms of apparatus designed for the production of nitrogen by this means have been patented. Of these the best known is the

Linde Nitrogen Separator.

In the article Oxygen, Fig. 1 illustrates the Linde oxygen separator, and in the description of that apparatus it is shown how it is possible to obtain pure liquid oxygen at the bottom of the rectification column, whilst the nitrogen vapours leaving the top of the column can never contain less than 7 p.c. of oxygen. Reference is also made to a modification of the Linde process due to Claude, by means of which small quantities of pure nitrogen may be obtained from an oxygen separator. For the production of pure nitrogen in large quantities, Linde employs a modified construction of his separator, which is illustrated diagrammatically in Fig. 2.

In this apparatus, as in the oxygen one, the circular upper portion of the casing is made of wood and contains in its centre the rectification column A, whilst the base, constructed of wood in the form of a hexagon, contains the vaporising or distilling chamber B. All clearance spaces are packed with sheep's wool, or other suitable insulating material in order to prevent the penetration of heat from the outside. C is the counter-current interchanger, constructed in the form of a large copper spiral pipe, and containing three smaller pipes of different sizes *d*, *e*, and *f*. The vertical pipe C is an extension of the main spiral pipe to the top of the rectification column A. The pipe coil d_1 shown in the vaporising chamber is connected at one extremity with pipe *d* contained in the counter-current interchanger. The other extremity of this pipe is connected to the inlet of the valve box G to the outlet of which another pipe d_2 is connected, as shown. This pipe is carried upwards and enters the rectification column near the middle, where it is fitted as shown with a rose-end, the function of which will be explained later. The coil f_1, also shown in the vaporising chamber, is connected at one extremity with the pipe *f* contained in the counter-current interchanger. The other extremity of this pipe is connected to the inlet of the valve box H to the outlet of which another pipe f_2 is connected, as shown. This pipe is carried upwards and enters the rectification column near the top, where it is fitted, as shown, with a rose-end, the function of which will be described later. The short pipe e_1 communicates at one end with the top of the vaporising chamber and is connected at the other end to the extremity of the pipe *e* contained in the counter-current interchanger.

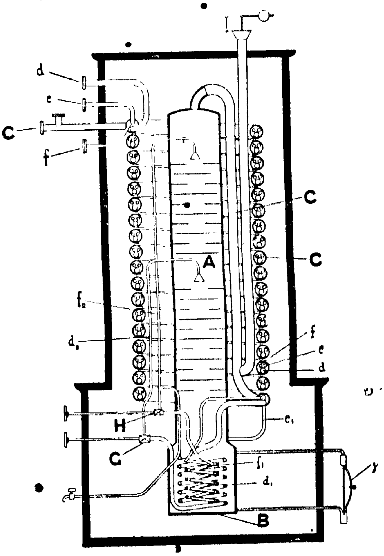


Fig. 2.

Two gas compressors are employed in conjunction with the separator, one working at high pressure and the other at low pressure. A fore-cooler as described in connection with the oxygen separator (v. Oxygen) may also advantageously be used. This fore-cooler is kept cold by means of a carbonic acid or ammonia machine, and is interposed between the compressors and the separator, so that the compressed gases leaving the compressors at normal atmospheric temperatures, become reduced to a temperature well below the freezing-point of water before they enter the separator. With this preliminary description of the essential parts, the working of the apparatus can now be readily followed.

There are, as in the case of all such apparatus, two stages in the working.

First, the preliminary cooling down and production of liquid, and *second* the separation of pure nitrogen.

The preliminary cooling may be effected by charging the vaporiser B with liquid air, separately produced; or air at normal atmospheric temperature (or less where a fore-cooler is employed) and at a pressure of about 2000 lbs. per square inch is conveyed from the high-pressure gas compressor through the small pipe *f* of the counter-current interchanger. (Although only one pipe *f* is shown, several of these are generally employed.) This compressed air then passes through the pipe coil f_1 in the vaporiser B to the inlet of the valve box H. At this point, by the adjustment of the valve spindle, the air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose-ended pipe f_2 into the top of the rectification column. This expanded air fills the column and flows away through the outlet C into the counter-current interchanger in a reverse flow to the incoming high pressure air, leaving the apparatus through the pipe C. As a branch of this pipe is coupled to the intake of the high-pressure compressor, it is obvious that the same air circulates through the apparatus with a regenerative cooling effect, until a temperature is ultimately reached at which the expanded air begins to liquefy and collect in that state round the coils in the vaporiser B. The quantity of liquid thus collected is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube *g* enclosed in a pressure-equalising circuit, as indicated.

When the vaporiser B is nearly filled with liquid, the second stage is reached in which the apparatus can be employed for the continuous production of nitrogen.

During the production of liquid in the vaporiser B, separation of oxygen and nitrogen has been taking place, first through simple fractional evaporation, and subsequently through rectification, as fully described under OXYGEN.

The nitrogen issuing from the pipe C has also been getting steadily purer in quality owing to the fact that it has been undergoing continuous treatment in an enclosed circuit. For the continuous production of pure nitrogen, it is, however, necessary to introduce a supplementary supply of liquid air, and as it is impossible by simple rectification to disengage nitrogen vapours from liquid air with less than 7 p.c. of oxygen, further treatment of the nitrogen has obviously to be employed in order to eliminate the residual oxygen. This is effected in the following manner:—

The air to be treated is supplied by the low-pressure compressor, already referred to, at normal atmospheric temperature (or less), and at a pressure of about 60 lbs. per square inch through the pipe *d* of the counter-current interchanger. This low-pressure air, thus cooled nearly to its temperature of condensation, then passes through the pipe coil d_1 in the vaporiser B, where its latent heat is transferred to the surrounding liquid, and it is itself entirely condensed, whilst at the same time evaporating an approximately equal quantity of the surrounding liquid. The pressure is then reduced by means of the valve G, and the liquid at atmospheric pressure is discharged into the lower part of the rectification column through the rose-ended pipe d_2. It is there rectified by the ascending vapours from the chamber B to a content of 7 p.c. of oxygen, whilst the liquid descending into the vaporising chamber is nearly pure oxygen. The nitrogen containing 7 p.c. of oxygen rises to the top of the column and is discharged from the apparatus through the pipe C and the main pipe C of the counter-current interchanger. Now, as already explained, a branch of the pipe C is coupled to the intake of the high-pressure compressor. Part of the outflowing nitrogen therefore enters that compressor, and passing through the high-pressure circuit in the manner already described, is liquefied and discharged at the top of the rectification column through the rose-ended pipe f_2. This liquid containing 7 p.c. of oxygen is, according to Baly's experiments (*v.* Fig. 3, OXYGEN), able to purify the vapours encountered by it down to about 2 p.c. of oxygen. Part of these are again drawn into the high-pressure system and condensed, and flowing into the column, continue automatically to displace oxygen from the rising vapours until pure nitrogen only is discharged from the pipe C. Part of this nitrogen continues to circulate through the high-pressure system for scrubbing purposes, but the major part is collected for use through the vertical branch on the pipe C. Oxygen vapours are abstracted from the apparatus through the pipes e_1 and *e*.

It is found that an installation of this description will produce approximately one cubic metre of nitrogen per ½ I.H.P.

(B) *By Chemical Means.*—(1) By passing chlorine through a strong solution of ammonia

$$8NH_3+3Cl_2=6NH_4Cl+N_2$$

The ammonia must be in excess, otherwise nitrogen chloride may be formed. Anderson (Chem. News, 5, 246) states that so obtained the nitrogen always contains oxygen. Ammonia is removed by passing through sulphuric acid.

(2) By adding metallic zinc to fused ammonium nitrate.

(3) By heating ammonium nitrite, or a mixture of ammonium chloride, and potassium nitrite: $NH_4NO_2=2H_2O+N_2$. This method gives nitric oxide in small quantity. If this is removed by ferrous sulphate solution, some is always evolved again on shaking, whilst with potassium permanganate oxygen is liberated in varying quantities (*v.* Knorre, Chem. Zentr. 1903, [i.] 125). The best method of procedure is to take 1 part $NaNO_2$, 1–2 parts $(NH_4)_2SO_4$, and 1 part $K_2Cr_2O_7$, warm the solution, and wash the gas evolved with a solution of 5 vols. saturated $K_2Cr_2O_7$ solution and 1 vol. concentrated H_2SO_4.

(4) By heating ammonium dichromate, or a mixture of ammonium chloride and potassium dichromate $(NH_4)_2Cr_2O_7=Cr_2O_3+4H_2O+N_2$.

(5) By heating glycerol (2 parts) and NH_4NO_3 (1 part) (Mai, Ber. 1901, 34, 3805).

The reaction commences at 190°, but once started proceeds without further heating till the temperature has fallen to 150°. A few drops of sulphuric acid cause the reaction to proceed more regularly and at a lower temperature. CO_2 is present in small quantity. The yield of nitrogen is nearly theoretical.

(6) By heating a mixture of dry ammonium nitrate and ammonium chloride

$$4NH_4NO_3+2NH_4Cl=Cl_2+12H_2O+5N_2$$

(7) By passing a mixture of (*a*) nitric oxide, or (*b*) nitrous oxide, with ammonia over heated copper gauze or platinised asbestos. The nitrogen is purified by passing through dilute H_2SO_4, over fused KOH, through concentrated H_2SO_4, and finally over red-hot copper gauze (Baxter and Hickey, Amer. Chem. J. 1905, 33, 300).

(8) By decomposing chamber crystals with ammonium sulphate at 130° (Pelouze, Ann. Chim. Phys. 1841, [iii.] 2, 49).

$$2NO_2{\cdot}SO_3H+(NH_4)_2SO_4=3H_2SO_4+2H_2O+2N_2$$

It is also formed in other chemical decompositions, notably by the action of hypochlorites and hypobromites on ammonia and acid amides, and of nitrous acid upon amines.

Spongy platinum boiled with ammonium sulphate and sulphuric acid gives SO_2 and N_2 (Delépine, Compt. rend. 1905, 141, 886), probably in accordance with the following equations—

(1) $4H_2SO_4+Pt=Pt(SO_4)_2+2SO_2+4H_2O$
(2) $3Pt(SO_4)_2+2(NH_4)_2SO_4=2N_2+3Pt+8H_2SO_4$

This explains the loss of nitrogen when platinichlorides of organic bases are estimated by the Kjeldahl method.

Properties.—Nitrogen is a colourless, inodorous, tasteless, neutral gas. Its density has been determined by many observers (*v.* Ramsay, Chem. News, 1899, 79, 13), and the discrepancy between the densities of atmospheric and chemically prepared nitrogen led to the discovery by Rayleigh of argon.

The density (air=1) and weight of 1 litre at N.T.P. are respectively 0·96737 and 1·25092 (Rayleigh, Proc. Roy. Soc. 1898, 62, 209), 0·96717 and 1·25070[1] (Leduc, Compt. rend. 1898, 126, 413), these giving for H=1 the values 14·002 and 14·004 respectively (Leduc, *ibid.* 1908, 146, 399). Rayleigh's later determinations (Proc. Roy. Soc. 1904, 73, 153) give the densities (H=1) at atmospheric and at very low pressures as 14·003 and 14·009 respectively.

The density of atmospheric nitrogen (containing the inert gases) is 0·97209 (Rayleigh, *l.c.*)

B.p. −195·0° (Dewar, *ibid.* 1902, 69, 360); −195·9 (Grunmach, Sitzungsber. K. Akad. Wiss. Berlin, 1906, 679); −195·55 (Alt, Ann. Physik. 1906, [iv.] 19, 739)

Olzewski (Compt. rend. 1884, 99, 133) gives the b.ps. at high pressures as follows—

P. in atm.	35	31	17
°C.	−146	−148·2	−160·5

See also Baly (Phil. Mag. 1900, [v.] 49, 517) and Fischer and Alt (Sitzungsber. K. Akad. München, 1902, 113).

	Baly	Dewar	Fischer and Alt.
M.p.	−210·52	−210·5	−210·48

Critical pressure 32·29 atm., critical temperature −146·25° (Wroblewski, Compt. rend. 1885, 100, 979), 33·49 atm. and −137·13° (Crommelin, Proc. K. Akad. Wetensch Amsterdam, 1915, 17, 959). Critical volume 42·6 c.c.; critical density 0·0235 (Dewar, Proc. Roy. Soc. 1904, 73, 251).

Sp.gr. of liquid nitrogen.

°C.	Sp gr.	Observer
−195·93	0·8084	Inglis and Coates.
	0·8010	Baly and Donnan.
−195·5	0·8042	Dewar.
−198·3	0·8297	Inglis and Coates.
	0·8218	Baly and Donnan

Sp.gr. of solid nitrogen.

°C.	Sp gr.	Observer
−210·5	0·8792	Dewar.
−252·5	1·0265	Dewar.

Molecular volume at 0° abs. (calc.)=25·49 (Dewar, Proc. Roy. Soc. 1904, 73, 251). Specific volume at m.p. 221·3 c.c (*ibid.* 1902, 69, 360). Sp.ht. of liquid nitrogen for temperature range of −196° to −208° is 0·430±0·008 (Alt, Ann. Physik. 1904, [iv.] 13, 1010). Sp.ht. of gaseous nitrogen 0·2348 between 0° and 200° (Regnault); 0·2419 from 20° to 440°; 0·2464 from 20° to 630°; 0·2492 from 20° to 800° (Holborn and Austin, Sitzungsber. K. Akad. Wiss. Berlin, 1905, 175), and has a mean value $0{\cdot}2350+0{\cdot}000019\theta$ between 0° and θ° (Holborn and Henning, Ann. Physik. 1907, [iv.] 23, 809).

Latent heat of vaporisation at b.p. 50·4 cal. (Dewar, Proc. Roy. Soc. 1905, A, 76, 325); at b.p. 47·65, at −202°, 49·42, at −210°, 51·61 (Alt, Ann. Physik 1906, [iv.] 19, 739). The vapour pressure of pure liquid nitrogen between −191·88° (p=1·4727 atm.) and −148·85° (30·304 atm.) may be expressed by the formula

$$\log p=5{\cdot}76381-853{\cdot}522/T+54372{\cdot}3/T^2-1783500T^3$$

(Crommelin, *l.c.*).

Vapour pressure at m.p. 93·5 mm.; from Fischer and Alt's values of the vapour pressures near the m.p. the m.p. calculated by Ramsay and Young's method is −210·24°. For atmospheric nitrogen the vapour pressure at the m.p. is 90·2 mm., and the calculated m.p. is −210·47°. The lowering of 0·23° is brought about by argon (1·70 gram per 100 grams N) from which the molecular depression is calculated as 5·39 and from this the latent heat of fusion is 14·49 cal. (Estreicher, Bull. Acad. Sci. Cracow, 1903, 831).

Surface tension 8·514±0·02 dynes/cm. (Grunmach. Sitzungsber. K. Akad. Wiss. Berlin, 1906, 679). Tables showing variation of surface tension and density of liquid nitrogen with temperature are given by Baly and Donnan (Chem. Soc. Trans 1902, 907).

The available pressure, volume, and thermal data for nitrogen at low temperatures have been collected and analysed by Plank (Physikal. Zeitsch. 1910, 11, 633).

Coefficient of expansion of liquid nitrogen varies from 0·002996 at 11°–132° abs. under 6 mm. to 0·003674 at 100° abs. under 1000 mm. (Erdmann, Ber. 1906, 39, 1207), and that of gaseous nitrogen 0·003643 from 0° to 1067° (Jacquerod and Perrot, Compt. rend. 1904, 138, 1032). The compressibility of gaseous nitrogen has been studied by Regnault, Natterer, Cailletet, Amagat (Ann. Chim. 1893, [vi.] 29, 68, 505), and Rayleigh (Proc. Roy. Soc. 1905, 74, 446). For the data the original papers must be consulted.

For viscosity constants of pure and atmospheric nitrogen, *v.* Markowski (Ann. Physik. 1904, 14, 742).

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[1] Moles (J. chim. physique, 1922, 19, 283), as the result of the discussion of 29 determinations, calculates the weight of the litre of nitrogen at 0° and 760 mm. and 45° cal. to be 1·2507±0·0001 grams.

The inversion temperature of the Joule-Kelvin phenomenon for atmospheric nitrogen is 243° at 159 atm. and 163° at 30 atm. (Olzewski, Bull. Acad. Sci. Cracow, 1906, 792; *v.* also Porter, Phil. Mag. 1910, [vi.] 19,888). Refractive index of gaseous nitrogen 1·000297 (Ramsay and Travers. Zeitsch. physikal. Chem. 1898, 100, 25), and of liquid nitrogen 1·2053 (Liveing and Dewar, Phil. Mag. 1893, [v.] 36, 328; *v.* also Cuthbertson, Proc. Roy. Soc. 1910, 83, A, 151). Electromagnetic rotation 0·000127 (Kundt and Röntgen, Wied. Ann. 1880, 10, 257). For density, refractivity relationship, and dispersion of gaseous nitrogen at its boiling-point, *v.* Gerold, Ann. Physik. 1921, [iv.] 65, 82.

Solubility.—Liquid oxygen at −195·5° dissolves 458 times it volume, or 50·7 p.c. of its weight of gaseous nitrogen (Erdmann and Bedford, Ber. 1904, 37, 1184). The solution obeys Henry's law, and liquid nitrogen therefore has the normal molecular weight, although oxygen dissolved in nitrogen is associated (Inglis and Coates, Chem. Soc. Trans. 1906, 886). Grunmach, however, from its surface tension calculates its molecular weight in the liquid state to be 37·3 (Sitzungsber. K. Akad. Wiss. Berlin, 1906, 679).

Solubility in water.

Temp.	0°	10°	20°	30°	40°	50°
c.c. per litre	23·00	18·54	15·54	13 55	12·15	11·02

(Fox, Trans. Faraday Soc. 1909, 5, 68; *see* also Winckler, Zeitsch. physikal. Chem. 1892, 9, 171). For solubility in alcohol *see* Carius, Annalen, 1855, 94, 136; in petroleum *see* Gniewosz and Walfisz, Zeitsch. physikal. Chem. 1887, 1, 70; in glycerol and *iso*butyric acid *see* Drucker and Moles, *ibid.* 1910, 75, 405: in solutions of organic substances *see* Hüfner, *ibid* 1907, 57, 611.

Wood charcoal absorbs ten times as much nitrogen at −185° as at 0° (Dewar, Compt. rend. 1904, 139, 261).

Chemical properties.—Nitrogen is not combustible, and does not support combustion, and in the free state, is remarkable for its inactivity. It may, however, be made to unite directly with boron, silicon, magnesium, titanium, tantalum, and tungsten. It is absorbed by a mixture of magnesium powder and lime, and, under certain conditions, combines with hydrogen, oxygen, and carbon, as, *e.g.*, when a series of electric sparks is passed through oxygen and nitrogen gases standing over a solution of caustic alkali, when a nitrate of the metal is produced. Traces of nitric acid and ammonium nitrate are produced by burning hydrogen gas mixed with nitrogen in an atmosphere of air or oxygen. Nitrogen can unite with hydrogen to form ammonia when the gases are in the nascent state. Carbon and nitrogen unite directly when nitrogen gas or atmospheric air is passed over an ignited mixture of charcoal and potash, or charcoal and baryta.

Nitrogen reacts slightly with steam at 2000°: $N_2+2H_2O=2NO+H_2$ (Tower, Ber. 1905, 38, 2945).

A detailed account of the spectrum is given by Fowler and Strutt (*ibid.* 1911, 85, A, 377). For the spectrum of nitrogen, *v.* also Deslandres (Compt. rend. 1902, 134, 747), Mosengeil (Ann. Physik. 1906, [iv.] 20, 833), Walter (*ibid.* 1906, [iv.] 20, 327), Nasini and Anderlini (at 3000°, Gazz. chim. ital. 1906, 36, ii. 561), Purvis (in strong magnetic field, Proc. Camb. Phil. Soc. 1906, 13, 354), Angerer (at low temperatures, Ann. Physik. 1910, [iv.] 32, 549), Helm (long-waved portion, Zeitsch. wiss. Photochem. 1910, 8, 405), Wien (canal rays, Physikal. Zeitsch. 1910, 11,377), Croze (infra red, Compt. rend. 1910, 150, 860).

Nitrogen is an essential constituent of many of the most potent and valuable medicines, as well as of some of the most powerful poisons, *e.g.* quinine, morphine, prussic acid, and strychnine. The slight affinity existing between nitrogen and other elements gives a peculiar character to its compounds, many of which are extremely prone to decomposition. Many nitrogen compounds, especially those which contain the oxygenated radicle *nitryl* (NO_2), are highly explosive, as in the case of the picrates, certain azo compounds, gun-cotton, the fulminates of silver and mercury, nitroglycerine, &c.

Active nitrogen. When a stream of rarefied nitrogen is subjected to the action of the electric discharge from a Leyden jar the gas exhibits a brilliant yellow light which persists for some little time after the exciting discharge is discontinued. The luminous gas gives a characteristic spectrum showing green, yellow, and red bands of about equal intensity. If passed through a glass tube moderately heated at one point the glow disappears locally. If strongly heated the glow is permanently extinguished. Its brilliancy is increased during cooling by liquid air but at the coolest part it is finally extinguished. Nitrogen thus treated shows remarkable chemical activity. It reacts with hydrocarbons such as methane, pentane, and acetylene to form hydrocyanic acid, and converts mercury and metallic vapours into nitrides which, when treated with water or potassium hydroxide solution, yield ammonia. It combines with phosphorus, gives a bright blue flame with iodine vapour; sulphur and arsenic give faint blue and green flames respectively. With nitric oxide it produces nitrogen peroxide: $2NO+N=NO_2+N_2$. Carbon disulphide yields a blue polymeric nitrogen sulphide and a polymerised carbon monosulphide. Sulphur chloride gives ordinary yellow nitrogen sulphide. With methyl bromide, ethyl iodide, chloroform, ethylene, and ethylidene dichlorides it forms hydrogen cyanide. When chlorine is present cyanogen chloride is produced; benzene yields cyanobenzene.

It is remarkable that if the nitrogen is pure it does not become 'active' under the influence of the discharge. The presence of a trace of some foreign substance such as oxygen, methane, ethylene, the oxides of carbon, hydrogen sulphide, or mercury vapour is necessary to its production. As regards oxygen, the amount needed to produce the greatest effect gradually increases until it reaches a maximum of about 1 part in 750, after which the intensity of the glow decreases: a 2 p.c. admixture completely destroys it. Active nitrogen would appear to have no chemical action on oxygen or hydrogen. Its production by the discharge is of the nature of a reversible reaction: the concentration only attains a certain limit, which may be lowered if the conditions become less favourable. The gas should be at a low pressure, say a few mm. of mercury, since collision with ordinary nitrogen molecules tends apparently to destroy it. It is also to a great extent destroyed by an uncondensed electrical discharge (without jar) or a steady current produced, for example, by a high-tension continuous current dynamo (Strutt, Proc. Roy. Soc. 1911, A, 85; 1912, 86, 262; 87, 179; 1913, 88, 539; 1915, 91, 303; 1916, 92, 438; 1917, 93, 254; Tiede and Domcke, Ber. 1913, 46, 4095; 1914, 47, 420; Koenig and Elod, *ibid.* 1914, 47, 516; *ibid.* 523; Baker and Strutt, Ber. 1914, 47, 801, and 1049; Baker, Tiede, Strutt, and Domcke, *ibid.* 1914, 47, 2283; Strutt, J. Soc. Chem. Ind. 1918, 113, 200).

For a detailed account of the spectrum of active nitrogen, *see* Fowler and Strutt, Proc. Roy. Soc. 1911, A, 85, 377.

According to Max Frantz (Zeitsch. Elektrochem. 1919, 25, 297) the main constituent of active nitrogen is triatomic nitrogen N_3. It has probably an open chain structure, as indicated by the nitride formation and by the absence of azide production. On cooling it reacts with N to form N_2, and on heating it decomposes into N and N_6, which is present in the gas in very small quantities at very low temperatures.

For the effect of the collision of *a* particles upon atoms of nitrogen, *see* Rutherford, Phil. Mag. 1919, [vi.] 37, 571, *ibid.* 581.

Halides of Nitrogen.

Nitrogen fluoride was supposed by Warren (Chem. News, 55, 289) to be formed when a saturated aqueous solution of ammonium fluoride was electrolysed, oily drops being noticed at the negative pole, which exploded violently when connected with the positive pole or in contact with organic matter, glass, or silica. Ruff and Geisel (Ber. 1903, 36, 2677) find, however, that nitrogen fluorides do not exist; that electrolysis of ammonium fluoride gives only pure fluorine, and that Warren's substance was probably nitrogen chloride produced from ammonium chloride present as an impurity.

Nitrogen chloride NCl_3. First prepared by Dulong in 1812 by the action of chlorine on an aqueous solution of ammonium chloride

$$NH_4Cl+3Cl_2=NCl_3+4HCl$$

The reaction has been studied by Noyes and Lyon (Amer. Chem. J. 1900, 23, 460); Bray and Dowell (J. Amer. Chem. Soc. 1917, 39, 905). Balard (Ann. Chim. 1834, [ii.] 57, 225, prepared it by the action of hypochlorous acid on ammonium chloride. Ammonium sulphate is more suitable, and Hentschel (Ber. 1897, 30, 1434, 1792) by that of sodium hypochlorite on ammonium chloride. Anhydrous ammonia and anhydrous chlorine react together to form nitrogen chloride and ammonium chloride. A considerable proportion of the nitrogen chloride at first formed decomposes into nitrogen and chlorine, either directly or by interaction with ammonia (Noyes and Haw, J. Amer. Chem. Soc. 1920, 42, 2167).

It is also formed in the electrolysis of a concentrated ammonium chloride solution (Kolbe, J. pr. Chem. 1847, 41, 137), this being the method best suited for lecture experiments (*v.* Meyer, Ber. 1886, 21, 26; Hofer, Chem. Zeit. 1896, 20, 470).

By adding a calcium hypochlorite solution saturated with hydrochloric acid to ammonium chloride solution, and shaking with benzene, the NCl_3 formed is dissolved in the benzene (Hentschel, Ber. 1897, 30, 2642). According to Rai (Chem. News, 1918, 253) it can be prepared by the action of bleaching powder on a saturated solution of ammonium chloride at about 0° without the use of hydrochloric acid or a solvent such as benzene or carbon tetrachloride.

By covering 150 c.c. of carbon tetrachloride with a concentrated aqueous solution of ammonium chloride, and passing in chlorine gas with vigorous shaking, and then washing with water, a bright yellow solution of the substance is obtained.

It is a yellowish volatile very pungent smelling oil, the vapour of which strongly attacks the eyes and mucous membrane; sp.gr. 1·653, b.p. 71°. It detonates on being heated to 93°, or when brought into contact with organic matter, phosphorus, arsenic, ozone, and alkalis. Metals, and strong acids, resins, and sugar do not cause its explosion, which is, however, brought about by exposure to strong light. It reacts slowly with dilute ammonium chloride solution and more rapidly with a concentrated solution to give nitrogen and hydrogen chloride:

$$NH_4Cl+NCl_3=N_2+4HCl$$

It dissolves in benzene, ether, chloroform, carbon tetrachloride, and carbon disulphide, giving highly refracting sulphur-yellow solutions, fairly stable in the dark, but slowly decomposing in light. Its benzene solution has been used for chlorinating organic substances (Hentschel, *l.c.*; *ibid.* 1898, 31, 246). Nitrogen chloride is quantitatively converted by dry hydrogen chloride into ammonium chloride (Noyes). Heat of formation −38,477 cal. (Troost, Compt. rend. 1868, 69, 204). For the action of nitrogen chloride in carbon tetrachloride solution on reducing agents, *see* Dowell and Bray (J. Amer. Chem. Soc. 1917, 39, 896).

The formula NCl_3 was assigned to it by Dulong (Schweigger's J. Chem. Pharm. 1812, 8, 32), Bineau (Ann. Chim. 1845, [iii.] 15, 82), and Deville and Hautefeuille (Compt. rend. 1869, 69, 152). Davy (Phil. Trans. 1813, 103, 1, 242) found the chlorine to be in excess of that required for this formula. Porret, Wilson and Kirk (Gilb. Ann. 1814, 47, 56, 59), and Gladstone (Chem. Soc. Trans. 1854, 7, 51) concluded that hydrogen was present (the latter giving the formula as N_2HCl_4), but the methods of analysis were not accurate. Gattermann determined the chlorine directly by decomposing a weighed quantity of the carefully purified and dried substance with concentrated ammonia, thus forming ammonium chloride, in which the chlorine was estimated as silver chloride, the result closely agreeing with the formula NCl_3 (Ber. 1888, 21, 755; *v.* also Hentschel, *l.c.*). This formula was confirmed by Chapman and Vodden (Chem. Soc. Trans. 1909, 141), who determined the ratio of nitrogen to chlorine, and also proved the absence of hydrogen.

Seliwanoff (Ber. 1894, 27, 1012) represents its hydrolysis with water as follows—

$$NCl_3+3H_2O \rightleftarrows NH_3+3HClO$$

This explains the easy reduction to ammonia, and the apparently greater solubility in hydrochloric acid than in sulphuric acid or water, since hydrochloric acid destroys hypochlorous acid. This is confirmed by Chapman and Vodden by shaking the CCl_4 solution with moderately concentrated HCl, removing any NCl_3 from the aqueous solution, and distilling with KOH, when ammonia is obtained in quantity—

$$NCl_3+3H_2O \rightleftarrows NH_3+3HClO$$
$$HClO+HCl \rightleftarrows Cl_2+H_2O$$
$$NH_3+HCl \rightleftarrows NH_4Cl$$

Nitrogen bromide is said to be formed as a dark red highly explosive volatile oil by adding potassium bromide to nitrogen chloride under water, and is possibly formed in a manner similar to the chloride, but no definite compound has been isolated.

Nitrogen iodide was first prepared by Courtois, and has since been obtained in a variety of ways, viz. by digesting aqueous ammonia with powdered iodine (Stas) or alcoholic iodine solution (Serullas, Ann. Chim. 1829, [ii.] 42, 200), or a solution of iodine in *aqua regia*, or directly with iodine chloride in potassium iodide solution (Schonbein; Guyard, Compt. rend. 1883, 97, 526); from alcoholic ammonia and iodine solutions (Bunsen), and from ammonium iodide and bleaching powder (Gladstone, Chem. Soc. Trans. 1855, 51).

It forms copper-coloured crystals, light red by transmitted light, sp.gr. 3·5, very readily exploded by shock, warming, or exposure to strong light. It is never obtained free from hydrogen, and at low temperatures gives molecular compounds with varying quantities of ammonia, viz. $NI_3{\cdot}NH_3$, $NI_3{\cdot}2NH_3$, $NI_3{\cdot}3NH_3$, $NI_3{\cdot}12NH_3$ (Hugot, Ann. Chim 1900, [vii.] 21, 5; Ruff, Ber. 1900, 33, 3025). The compound $NI_3.NH_3$ is usually isolated, this formula representing its structure (Chattaway and Orton, Amer. Chem. J. 1900, 24, 331; Silberrad, Chem. Soc. Trans. 1905, 55).

Silberrad finds it to react with zinc ethyl as follows—

$$(1)\ NH_3{\cdot}NI_3+3Zn(C_2H_5)_2 =3ZnC_2H_5I+NH_3+N(C_2H_5)_3$$
$$(2)\ 2NH_3+Zn(C_2H_5)_2=Zn(NH_2)_2+2C_2H_6$$

According to Seliwanoff (Ber. 1894, 27, 1012) its hydrolysis with water is as follows—

$$NH_3{\cdot}NI_3+3H_2O \rightleftarrows 2NH_4IO+HIO$$

It is reduced by H_2S, SO_2, As_2O_3, similarly to NCl_3. Hydriodic acid liberates iodine, hydrochloric acid forms iodine chloride, hydrocyanic acid iodine cyanide, and alkalis a mixture of iodide and iodate. It reacts with organic iodides (Silberrad and Smart, Chem Soc. Trans. 1906, 172).

NITROGEN AND SULPHUR.

Nitrogen sulphide was first prepared by Fordos and Gélis (Compt. rend. 1850, 31, 702), who assigned to it the formula SN.

It is obtained by passing dry ammonia gas into a solution of sulphur dichloride in carbon disulphide or benzene

According to Francis and Davis (Chem. Soc. Trans. 1904, 259), it is best prepared from a 10–15 p.c. solution of S_2Cl_2 in benzene, into which a rapid current of dry ammonia is passed until red fumes appear, after which the liquid is cooled and the current continued for a short time longer. The ammonium chloride is filtered off, and on evaporation of the filtrate, orange-red prisms are obtained which, recrystallised from boiling benzene, toluene, or carbon disulphide, melt at 185°. It is more stable than previous observers have stated, its supposedly greater tendency to explode probably being due to impurities present, as indicated by the lower melting-points given by them (*cf.* Schenck, Annalen, 1896, 290, 171). It may be sublimed under reduced pressure. Crystallographic constants (Artini, Chem. Zentr. 1906, i. 1774)—

$$[a:b:c=0{\cdot}8806:1:0{\cdot}8430;\ \beta=89°\ 20']$$

Its formation is usually represented by the equation—

$$8NH_3+3S_2Cl_2=6NH_4Cl+2NS+S_4$$

but according to Ruff and Geisel (Ber. 1904, 37, 1573), the relation of the yield to the composition of the sulphur chloride employed indicates SCl_4 to be concerned in the reaction—

$$12SCl_4+16NH_3=3S_4N_4+48HCl+2N_2$$

Its molecular formula is S_4N_4 (Schenck, *l.c.*; Muthmann, Ber 1896, 29, 340; Francis and Davis, *l.c.*).

With chlorine in chloroform solution, the *tetrachloride* $N_4S_4Cl_4$ is formed, which crystallises on cooling in magnificent yellow crystals which decompose on heating—

$$N_4S_4Cl_4=2N_2+2S_2Cl_2$$

It is excessively unstable, giving a black tarry mass on exposure to moist air (Demarçay, Compt. rend. 91, 854; Muthmann and Seiter, Ber. 1897, 30, 627).

Demarçay also describes the compound $(SN)_3Cl$, as produced by adding the requisite proportion of nitrogen sulphide to the tetrachloride in chloroform solution. This is probably *thio-trithioazylchloride* N_3S_4Cl, obtained by the action of N_4S_4 upon S_2Cl_2 in chloroform solution, or by heating N_4S_4 with acetyl chloride. It is an intensely yellow crystalline powder, which explodes a few minutes after becoming dry. It readily absorbs ammonia.

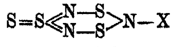
Muthmann and Seiter (*l.c.*) also describe the following derivatives—

Thio-trithioazylnitrate $N_3S_4NO_3$, obtained as sulphur yellow prisms when the chloride is dissolved in concentrated nitric acid and evaporated *in vacuô*. Its solution in water darkens after a few minutes, giving a black deposit. When dry it is very explosive.

Thio-trithioazylbromide N_3S_4Br is formed by the action of N_4S_4 on S_2Br_2 in CS_2 solution, or of bromine on the chloride in CS_2 solution, or by exposing the tetrabromide of nitrogen sulphide (prepared similarly to the chloride) to moist air. It is stable in air.

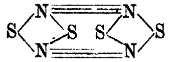
Thio-trithioazyliodide N_3S_4I is prepared from solutions of the chloride and potassium iodide in ice cold water. It is very unstable.

Thio-trithioazylthiocyanate N_3S_4CNS, from ice-cold solutions of the chloride or nitrate and potassium thiocyanate, forms lustrous bronze leaflets, fairly soluble in benzene and chloroform which resist the action of the air. These compounds have the constitution—

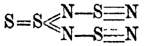


$$S{=}S\lessgtr\begin{matrix}N{-}S\\N{-}S\end{matrix}{>}N{-}X$$

Schenck assigns to N_4S_4 the constitutional formula—



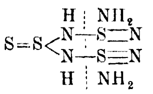
but Ruff and Geisel (*l.c.*) regard the divalence of the sulphur atoms as improbable, and suggest the formula—



$$S{=}S\lessgtr\begin{matrix}N{-}S{\equiv}N\\N{-}S{\equiv}N\end{matrix}$$

which is supported by its reaction with metallic iodides in anhydrous liquid ammonia. Lead iodide gives olive green prisms of the dithio-di-imide, $Pb{\cdot}N_2S_2{\cdot}2NH_3$, and mercury iodide bright yellow crystals of the thio-di-imide, $Hg{\cdot}N_2S{\cdot}NH_3$, but in neither case is precipitation complete, and the mother liquor from the lead salt gives the mercury compound with mercury iodide, whilst that from the mercury salt gives the lead compound with lead iodide. These facts are accounted for by the supposition that in ammonia solution dissociation of the above molecule takes place into the ions—

$$N{\equiv}S{\cdot}NH_2 \text{ and } S{=}S(NH)_2$$



$$S{=}S\lessgtr\begin{matrix}\overset{H}{N}{-}\overset{NH_2}{S}{\equiv}N\\\underset{H}{N}{-}\underset{NH_2}{S}{\equiv}N\end{matrix}$$

Nitrogen sulphide reacts with a number of metallic chlorides giving additive compounds (Wölbing, Zeitsch. anorg. Chem. 1908, 57, 281); with amines (Schenck, *l.c.*); with acetic acid and its halogen derivatives (Francis, Chem. Soc. Trans. 1905, 1836); with aromatic aldehydes (Davis, *ibid.* 1831); with hydrofluoric acid (Ruff and Thiel, Ber. 1905, 38, 549).

Stannous chloride does not combine, but on warming in benzene solution the N_4S_4 is reduced with formation of yellow lustrous leaflets, m.p. 152°, of the empirical formula NSH. It is not combustible or explosive. NH_3 is evolved on heating with KOH (Wölbing, *l.c.*).

According to Moissan (Compt. rend. 132, 510), the reaction $10S+4NH_3 \rightleftarrows 6H_2S+N_4S_4$ is reversible; nitrogen sulphide can be obtained from sulphur and ammonia in presence of silver iodide.

Dry HCl reacts as follows—

$$N_4S_4+12HCl=4NH_3+4S\underbrace{+12Cl}$$

showing that sulphur is united to nitrogen by 12 valencies, and hence, in agreement with Ruff and Geisel's formula, no N atoms are linked. Ht. of formation of N_4S_4 −81,900 cal. (Berthelot and Vieille, Ann. Chim. 1882, [v.] 28, 202).

A blue modification of the yellow sulphide N_4S_4 is described by Burt (Chem. Soc. Trans 1910, 1171) as obtained by subliming the latter over silver gauze. It is much less volatile, and evidently formed from an unstable intermediate reduction product which loses nitrogen.

A liquid sulphide N_2S_5 is obtained when N_4S_4 and CS_2 are heated together at 100° for two hours under 5 atm. pressure (Muthmann and Clever, Zeitsch. anorg. Chem. 1897, 13, 200).

OXIDES AND OXYACIDS OF NITROGEN.

Nitrous oxide. *Laughing gas*, N_2O. First obtained by Priestley in 1772, by the action of easily oxidisable substances, such as potassium sulphide or sulphite, on nitric oxide. NO is also reduced to N_2O by iron or zinc filings, or stannous chloride.

Nitrous acid and nitrites yield N_2O when reduced by platinum black, and by sodium amalgam.

Nitric acid and nitrates give N_2O among their reduction products with various reducing agents, especially from zinc and dilute nitric acid or a mixture of equal parts of nitric and sulphuric acids diluted with eight to ten parts of water.

It is usually supposed not to be formed by direct union, *v.*, however, method (6), *infra.* Warburg and Leithauser (Sitzungsber. K. Akad. Wiss. Berlin, 1908, 148) find that Siemen's ozoniser gives N_2O and N_2O_5, and that the spark between platinum electrodes gives NO_2 and N_2O, the alternating arc at high potential in dry air giving only NO_2.

Matignon from thermodynamical considerations infers that the direct union of nitrogen and oxygen with production of nitrous oxide should be realisible at 3000° and 3000 atmos. (Compt. rend. 1912, 154, 203).

No combination between nitrogen and oxygen is effected under the influence of ultraviolet light (Berthelot and Gaudechon, Compt. rend. 1910, 150, 1517).

The best methods in practice are—

(1) Campari's method (Chem. Zentr. 1888, 1569), by heating to boiling a mixture of 5 parts stannous chloride, 10 parts hydrochloric acid of sp.gr. 1·21, and 0·9 part of nitric acid of sp.gr. 1·38. These proportions should be adhered to, or the gas is liable to be evolved with explosive irregularity (*v.* also Gay Lussac, Ann. Chim. 1847, [iii.] 23, 229).

(2) By reduction of nitrous acid with hydrazine—

$$N_2H_4+HNO_2=NH_3+N_2O+H_2O$$

(Francke, Ber. 1905, 38, 4102).

(3) By decomposition of ammonium nitrate by heat; $NH_4NO_3=N_2O+2H_2O$. The decomposition begins at about 170°, and becomes explosive unless carefully regulated. Organic impurities must be absent, and also ammonium chloride, otherwise CO_2 and Cl_2 respectively are formed Soubeiran, J. Pharm. Chim. 1826, 13, 332).

Lidoff (J. Russ. Phys. Chem. Soc. 1903, 35, 59) recommends mixing the nitrate with sand, and washing the gas with ferrous sulphate solution, afterwards drying it with an emulsion of ferrous sulphate in concentrated sulphuric acid.

(4) By Thilo's method (Chem. Zeit. 1894, 18, 532), patented in 1894. An equimolecular mixture of ammonium sulphate and sodium nitrate is heated at 240°. A regular and quiet evolution of nitrous oxide results.

(5) By the reaction between sodium nitrite

and hydroxylamine hydrochloride solutions, NO being removed by ferrous sulphate solution—

$$NH_2OH+HNO_2=N_2O+2H_2O$$

(Meyer, Pollak's modification, Annalen, 1875, 175 141).

(6) Pictet (Fr. Pat. 415594, April 19, 1910) and Södermann (*ibid.* 411785, Jan. 21, 1910) obtain it from the nitrogen-oxygen flame, produced electrically or by other means, under suitable conditions. At a definite part of the flame, ascertained spectroscopically or in other ways, the chief product is N_2O, and by rapid and efficient cooling at this point the gas may be obtained in 25 p.c. yield.

Properties.—Nitrous oxide is a colourless gas with pleasant odour and sweetish taste. Density (air=1) 1·5301 (Leduc, Compt. rend. 1905, 140, 642), 1·5297 (Rayleigh, Proc. Roy. Soc. 1905, 74, 181). Weight of one litre 1·9774 grams (Guye and Pintza, Compt. rend. 1905, 141, 51), 1·9777 (Rayleigh), 1·9780 (Leduc).

Coeff. of expansion 0·0037067 (Jolly). For its volume-pressure relations, *v.* Rayleigh (Proc. Roy. Soc. 1905, 74, 406).

Viscosity coeff. 0·0001353 at 0°; 0·0001815 at 100° (Wullner, Wied. Ann. 1876, 4, 321).

Refractive index for sodium light 1·00516. Magnetic rotation 16·02 (Becquerel, Compt. rend 1880, 90, 1407; *v.* also Dufour, *ibid.* 1908, 147, 1471). Sp.ht. at const. vol. 0·15130 at 0°; 0 17384 at 100° (Wüllner, *l c.*). Sp.ht. at const press. 0·1983 at 0°; 0·2212 at 100° (Wiedermann, Pogg. Ann. 1875, 157, 1).

Cp./Cv.=1·31 at 0°; 1·2724 at 100°.

Cf. Mercer, Proc. Physical Soc. 1914, 26, 155. Heuse (Ann. Physik. 1919, [iv.] 59, 80) finds Cp. 20°, 0·879; −30°, 0·835; −70°, 0·797. Heat conductivity 0·0000350 at 0°; 0 0000506 at 100°.

It is easily liquefied, and was first obtained in liquid form by Faraday (Phil. Trans. 1823, 189). The liquid is colourless, mobile, and has a low refractive index (1·193 at 16°, according to Bleikrode, 1·3305 at 90°, according to Liveing and Dewar); b.p. −89·8° (Ramsay and Shields, Chem. News, 1893, 67, 190; −89·4° (Grunmach, Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1198); −88·7° (Burrell and Robertson, J. Amer. Chem. Soc. 1915, 37, 2691); m.p. −102·3° (Ramsay and Shields, *l.c.*). Crystallises in forms belonging to the cubic system (Behnken). Critical temp. and press. 36·4°, 73·07 atm. (Cailletet and Matthias); 35·4° and 75·0 atm. (Dewar. Phil. Mag. 1884, [v.] 18, 210); 36·5° and 71·65 atm. (Cardoso and Arni, J. Chem. Phys. 1912, 10, 504).

Density at b.p. 1·2257 (Grunmach). Surface tension at 89·3°, 26·323 dynes/cm. Calculated molecular weights using the critical values given above are 43·26 and 43·78 respectively, hence N_2O has the same molecular weight in both states (Grunmach). The vapour pressures are tabulated by Regnault (J. 1863, 70) and Villard (Ann. Chim. 1897, [vii.] 10, 387). Vapour pressures of solid nitrous oxide between −90 6° and −144·1° may be represented by the equation $\log p=-1232\cdot2/T+9\cdot579$ (Burrell and Robertson (J. Amer. Chem. Soc. 1915, 37, 2691).

For densities of liquid N_2O and its saturated vapour, *v.* Cailletet and Mathias (Compt. rend. 1886, 102, 1202; Villard (*ibid.* 1894, 118, 1096).

Mol. heat of volatilisation 2900 cal. (−20°), 2600 (0°), 400 (35°) (Cailletet and Mathias, Ann. Chim. 1890, [vi.] 21, 69). Heat of formation −21,700 cal,

Solubility in water at	5°	10°	15°	20°	25°
	1·048	0·8778	0·7377	0·6294	0·5443

(Geffcken, Zeitsch. physikal. Chem. 1904, 49, 257).

Findlay and Creighton (Chem. Soc. Trans. 1910, 549); Findlay and Howell (*ibid.* 1914, 291) show that it obeys Henry's Law.

$$\text{At } 25^\circ \quad \frac{\text{Conc. liquid phase}}{\text{Conc. gaseous phase}}=0\cdot585$$

For the influence of colloids on its solubility, *see* Findlay and Howell (*l.c.*). For its solubility in alcohol, *v.* Carius (Annalen, 1855, 94, 139).

Nitrous oxide is an endothermic compound, and is decomposed into its elements on strongly heating. This is shown by its power to support the combustion of phosphorus, carbon, sulphur, &c., when burning sufficiently vigorously to start the decomposition of the gas. At 500°, only about 1·5 p.c. is decomposed, but at 900° decomposition is practically complete. Hunter (Zeitsch. physikal. Chem. 1905, 53, 441) finds its decomposition to be mainly bi-molecular, $2N_2O=2N_2+O_2$, and gives the velocity coefficients at various temperatures. It also decomposes slightly under pressure. At 600 atm. and 420°, slight decomposition occurs with increase in volume (Briner and Wroczynski, Compt. rend. 1910, 150, 1324).

Mixed with oxygen and submitted to the action of ultra-violet light it gives nitrogen and higher oxidation products (Berthelot and Gaudechon, Compt. rend. 1910, 150, 1517). Mixed with carbon disulphide it burns with a blue actinic flame.

It is readily reduced by hydrogen on passing the mixed gases through a red-hot tube, or over platinum or palladium sponge. It is analysed by explosion with hydrogen (Hempel, Zeitsch. Elektrochem. 1906, 12, 600). The velocity of explosion is 2305 metres per sec. (Dixon, Chem. News, 1891, 64, 70). It oxidises a large number of metals and lower oxides, and reduced nickel brings about its reduction with hydrogen to water and nitrogen (Sabatier and Senderens, Compt. rend. 1902, 135, 278). Potassium and sodium, when slightly heated in the gas, form the peroxides, but when strongly heated produce the nitrates.

Nitrous oxide is a valuable anæsthetic for short operations. Prolonged inhalation causes death. Mixed with about one-fourth its volume of oxygen it produces an exhilarating and intoxicating effect. For a discussion of its preparation and requisite purity for use as an anæsthetic, *v.* Baskerville and Stevenson (J. Ind. Eng. Chem. 1911, 3, 579).

Liquid nitrous oxide is obtainable in steel cylinders holding up to about 50 lbs., equivalent to 430 cb. ft. of gas. For anæsthetic purposes the gas should be free from chlorine, other oxides of nitrogen, &c., and should contain at least 95 p.c. nitrous oxide.

Hyponitrites may be regarded as salts of this oxide, though the acid is not formed by its solution in water. At low temperatures a solid hydrate $N_2O{\cdot}6H_2O$ is formed (Villard, Ann. Chim. 1897, [vii.] 11, 289).

Nitric oxide NO differs from the other oxides in being neither an acid anhydride as N_2O, N_2O_3 and N_2O_5, nor a mixed anhydride, as N_2O_4. It was the first oxide of nitrogen investigated (Priestley, 1772).

It is usually said to be the first oxidation product of elementary nitrogen (*v.*, however, *Nitrous oxide*) and is formed by direct union by a number of methods. It is produced together with ozone in the silent electric discharge, and has an inhibiting effect upon the formation of ozone (Manchot, Ber. 1908, 41, 471).

It is produced (also along with ozone) when air is slowly led over a glowing Nernst filament (Fischer and Marx, Ber. 1906, 39, 3631), and in various flames, *e.g.* C_2H_4, CO, and H_2, as well as in the electric arc, electric spark, and at white-hot solid surfaces (Haber and Coates, Zeitsch. physikal. Chem. 1909, 69, 337).

In the combustion of hydrogen in air at ordinary pressures, practically no nitric oxide is formed, but at 20 atm. 0·3 molecule of NO is produced for every 100 mols. of water. With equal mixtures of N_2 and O_2, the yield though small at low pressures is as much as 3 mols. per 100 of water at 15 atm. (Wolokitin, Zeitsch Elektrochem. 1910, 16, 814).

The conditions under which the union is most efficient have been studied by Haber and his co-workers (*v.* Haber and others, Zeitsch. Elektrochem. 1910, 16, 810, and earlier papers), Nernst and others (Fischer and Hene, Ber. 1912, 45, 3652; 1913, 46, 603; Koenig, Ber. 1913, 46, 132; Gorbov and Mitkevitsch, J. Russ. Phys. Chem. Soc. 1913, 45, 1109). Briefly, a high temperature favours a rapid rate of formation, and a high yield of NO, but also favours dissociation. Hence rapid cooling is necessary at the moment of formation, which is realised by sweeping the gases out of the region of the arc, or by forming and interrupting the arc successively several thousand times a second, or by playing the arc in different regions of the space. The gases passing out of the chamber contain 1–2 p.c. of NO by volume. For practical details, *v.* NITROGEN, ATMOSPHERIC, UTILISATION OF.

For a study of the changes in nitric oxide in a methane-oxygen flame, *see* Reis and Waldbauer, Zeitsch. physikal. Chem. 1913, 85, 62.

Nitric oxide is also produced by the action of a variety of reducing agents upon nitric and nitrous acids and the higher oxides.

The most convenient methods are—

(1) Nitric acid of sp.gr. 1·2 on metallic copper.

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$$
$$(3Cu+N_2O_5=3CuO+2NO)$$

(*v.* Kämmerer, Ber. 1885, 18, 3064; *cf.* Rennie and Cooke, Chem. Soc. Trans. 1908, 93, 1162; *ibid.* 1911, 99, 1035; Stansbie, J. Soc. Chem. Ind. 1913, 319).

(2) An alkaline nitrate on a solution of ferrous chloride in hydrochloric acid.

$$6FeCl_2+2NaNO_3+8HCl$$
$$=6FeCl_3+2NaCl+4H_2O+2NO$$

(Pelouze; Gay Lussac, Ann. Chim. 1847, [iii.] 23, 203).

(3) Deventer's method (Ber. 1893, 26, 589) of dropping a mixture of potassium nitrite and ferrocyanide into dilute acetic acid.

$$K_4Fe(CN)_6+HNO_2+CH_3COOH$$
$$=K_3Fe(CN)_6+H_2O+CH_3COOK+NO$$

(4) Dropping 50 p.c. sulphuric acid into a concentrated solution of potassium iodide and sodium nitrite in molecular proportions.

(5) Aqueous ferric chloride on sodium nitrite.

$$FeCl_3+3NaNO_2=Fe(NO_2)_3+3NaCl$$
$$2Fe(NO_2)_3+3H_2O=2Fe(OH)_3+3NO_2+3NO$$

If the $NaNO_2$ is placed under carbon disulphide and hydrated $FeCl_3$ in carbon disulphide suspension added, the NO_2 remains dissolved in the carbon disulphide (Matuschek, Chem. Zeit. 1905, 29, 31).

(6) SO_2 into warm HNO_3 of sp.gr. 1·15.

$$3SO_2+2HNO_3+2H_2O=2H_2SO_4+2NO$$

(Weber, Pogg. Ann. 1867, 130, 277).

Moser (Zeitsch anal. Chem. 1911, 50, 401) considers the best methods are—

(*a*) Reduction of HNO_2 in H_2SO_4 with Hg.

(*b*) Reduction of HNO_2 with HI.

The gas is purified by absorption in concentrated ferrous sulphate solution, from which it is expelled again on gently heating. It is also absorbed by potassium permanganate or dichromate.

Nitric oxide is readily obtained by the electrolysis of a mixture of nitric and nitrous acids with a current of 5–10 amperes at the ordinary temperature (D. R. P. 244362).

Properties.—Nitric oxide is a colourless gas, of density 1·0387 (Leduc, Compt. rend. 1893, 116, 322). Wt. of one litre at N.T.P. 1·3402 (Gray, Chem. Soc. Proc. 1903, 56; Guye and Davila, Compt. rend. 1905, 141, 826). Cp. 0·23175 (Regnault), Cp./Cv. 1·40. Coeff. of expansion (mean) between −140° and 0°, 0·0037074 (Adventowski, Bull. Acad. Sci. Cracow, 1909, 742). Viscosity coeff. 0·000168 (Meyer and Springmühl, Pogg. Ann. 1873, 148, 526).

Refractive index for white light 1·000303 (Dulong) · for sodium light 1·000297 (Mascart, Zeitsch. physikal. Chem. 1891, 7, 25), 1·0002939 (Cuthbertson and Metcalfe, Proc. Roy. Soc. 1908, A, 80, 406).

Nitric oxide shows very little divergence from Boyle's law (Jacquerod and Schener, Compt. rend. 1905, 140, 1384). It is with difficulty condensed to a colourless liquid.

B.p.	M.p.	Crit. temp.	Crit. press.	Observer
−153·6°	−167·0°	−93·5°	71·2atm.	Olzewski[1]
−150·2°	−160·6°	−92·9°	64·4atm.	Adventowski

For b.pts. at pressures other than atmospheric, *v.* Olzewski (*l.c.*). V.p. at m.p. 168 mm.

The vapour pressure curve of the liquid would appear to indicate that polymerisation of the molecules takes place at very low temperatures. This is borne out by the high sp.gr. of the liquid at its b.p. (1·269) (Adventowski, *l.c.*).

Heat of formation of NO −21,575 cal. (Thomsen), −21,600 cal. (Berthelot, Compt. rend. 1874, 78, 162). Sp. heat Cp. 15°, 1·012; −45°, 1·001; −55°, 1·014; −80°, 1·024 (Heuse, Ann. Physik. 1919, [iv.] 59, 86).

[1] Compt rend. 1885, 100, 940.

SOLUBILITY IN WATER.

°C.	Absorption coeff.	°C.	Absorption coeff.
0	0·07381	40	0·03507
5	0·06461	50	0·03152
10	0·05709	60	0·02954
15	0·05147	70	0·02810
20	0·04706	80	0·02700
25	0·04323	90	0·02648
30	0·04004	100	0·02628

(Winkler, Ber. 1901, 34, 1408; *v.* also Zeitsch. physikal. Chem. 1892, 9, 171).

It is more soluble (0·316 at 0°) in alcohol (Carius, Annalen, 1885, 94, 138). For its solubility in H_2SO_4, *v.* Lunge (Ber. 1885, 18, 1391); Tower (Zeitsch. anorg. Chem. 1906, 50, 382).

Nitric oxide is the most stable oxide of nitrogen. At 700° only 0·5 p.c. is dissociated into nitrogen and oxygen, and at 1000° only 3–4 p.c. The dynamics of the equilibrium have been studied by Muthmann and Hofer (Ber. 1903, 36, 438); Nernst (Zeitsch. anorg. Chem. 1906, 49, 213); Jellinek (*ibid.* 1906, 49, 229), and Brode (Zeitsch. Elektrochem. 1905, 11, 752). Briner and Boubnoff (Compt. rend. 1913, 156, 228) have studied the decomposition of nitric oxide over wide ranges of pressure (50–700 atmos.) and temperature (−90°–300°). Nitrogen, nitrous and nitric oxides, and nitrogen trioxide and peroxide were found among the products. The main reactions are (1) $2NO=N_2+O_2$, and (2) $4NO=2N_2O+O_2$, the second predominating, the higher oxides being formed by the secondary action of oxygen on the untransformed nitric oxide, *cf.* Guye and Schneider, (Helv. Chim. Acta, 1918, 1, 33).

At ordinary temperatures it combines with oxygen with production of ruddy fumes (*v.* Emich, Monatsh. 13, 86) characteristic of the peroxide, but at the temperature of liquid air the product is always nitrogen tetroxide, whatever the proportions taken, even if both the oxygen and nitrogen are in the gaseous state provided the temperature be below −110°. N_2O_3 is transformed by oxygen to N_2O_4 only above −100°, and N_2O_4 is reduced by NO to N_2O_3 at temperatures below −150° (Francesconi and Sciacca, Gazz. chim. ital. 1904, 34, i. 447). *Cf.* Raschig (Verh. Ges. deut. Naturforsch. Aerzte, 1912, ii. [i.] 199), who infers the existence of a nitrogen hexoxide NO_3. According to Sanfourche (Compt. rend. 1919, 168, 307 and 401) the first stage in the oxidation of nitric oxide, $4NO+O_2=2N_2O_3$, is practically instantaneous and independent of the temperature between −50° and 525°. The second stage, $2N_2O_3+O_2 \leftrightarrows 4NO_2$, is reversible. Up to 200° it tends from left to right, but from 200° to 525° it tends more and more from right to left as the temperature rises. In presence of water nitric oxide is oxidised to nitrogen trioxide and not the peroxide, the trioxide then being decomposed by the water, with formation of nitric acid and partial regeneration of nitric oxide. In presence of concentrated nitric acid (sp.gr. 1·5) the nitrogen trioxide is oxidised, forming nitrogen peroxide and water:

$$2HNO_3+N_2O_3=2N_2O_4+H_2O$$

If dilute nitric acid is used the action is the same as with water, until the acid is concentrated to about 50 p.c. (sp.gr. 1·3), when the second reaction takes place and increases with the concentration of the nitric acid. For velocity of oxidation of nitric oxide, *see* Bodenstein, Zeitsch. Elektrochem. 1918, 24, 183; Briner and Fridövi, Helv. Chim. Acta, 1918, 1, 181; Trautz, Zeitsch. Elektrochem. 1919, 25, 4; Wourtzel, Compt. rend. 1920, 170, 109; *ibid* 229. Nitric oxide may be reduced in a variety of ways, giving nitrogen, ammonia, and in a few instances nitrous oxide. Hydrogen sulphide and alkaline sulphides, sulphurous acid, and phosphine give N_2O largely. Metals reduced in hydrogen are readily oxidised at a low temperature with formation of nitrogen. Passed with hydrogen over nickel, ammonia and some nitrogen are produced (Sabatier and Senderens, Compt. rend. 1902, 135, 278). The reaction commences at 300° and then proceeds at 120°, the production of ammonia being almost quantitative (Neogi and Adhicány, Zeitsch. anorg. Chem. 1910, 69, 209).

With hydriodic acid, ammonia is produced. Stannous chloride gives hydroxylamine and ammonia (Chesnau, Compt. rend. 1899, 129, 100) and in alkaline solution hyponitrite as well. Chromous salts give ammonia in neutral solution, hydroxylamine in acid solution (Kohlschutter, Ber. 1904, 37, 3053). Alkaline pyrogallol reduces it to nitrous oxide (Oppenheimer, *ibid.* 1903, 36, 1744).

It also reacts with oxidising agents. H_2O_2 gives nitrous and nitric acids; PbO_2, Pb_3O_4, MnO_2, Ag_2O in water give nitrite; $KMnO_4$ gives nitrate; iodine nitric acid (Schonbein), ClO_2 gives N_2O_4, and hypochlorous acid nitric acid (Balard).

In the dry state it acts on many oxidising agents, forming nitrite and nitrate (Auden and Fowler, Chem. News, 1895, 72, 163). It gives N_2O_3 with N_2O_4 at low temperatures (*v.* under *Nitric trioxide*).

It is slowly decomposed by potash, forming KNO_2 and N_2 (*v.* also Emich, Monatsh. 1892, 13, 90), and according to Moser (Zeitsch. anal. Chem. 1911, 50, 401) it cannot be preserved unchanged over water, partly owing to dissolved oxygen, and partly to hydrions of the water

$$4NO+2H_2O=2HNO_2+H_2N_2O_2$$

(*cf.* Zimmermann, Monatsh. 1905, 26, 1277).

The latter gives N_2O, and also ammonium nitrite, $3H_2N_2O_2=2N_2O_3+2NH_3$ (*cf.* Hantzsch and Kauffmann, Annalen, 1896, 292, 317), which further breaks down giving nitrogen in increasing quantity with the length of time the gas remains over water. The moist gas can, however, be preserved unchanged over mercury.

It can be catalytically decomposed by finely-divided nickel suspended in hot water with the production of nitrogen and nickel oxide (Felgate, Chem. News, 1913, 108, 178). A mixture of hydrogen and nitric oxide in the ratio 3 : 1 passed over finely divided tin, reduced iron, or zinc-dust when heated gives an almost quantitative yield of ammonia (Adhikary, Chem. News, 1915, 112, 163). Guye and Schneider (Helv. Chim. Acta, 1918, 1, 33) find that in the reduction of nitric oxide with nickel as catalyst two reactions take place simultaneously, the one giving ammonia and the other nitrogen:

$$(1)\ 2NO+5H_2=2NH_3+2H_2O$$
$$(2)\ 2NO+H_2=N_2+H_2O$$

No nitrous oxide is formed. Temperatures of 250°–300° appear to be the best for the production of ammonia. 70 p.c. of the gas is transformed into ammonia.

Fluorine gives NO_2F (*q.v.*); iodine does not react; chlorine and bromine give the corresponding halide (*v.* under *Nitrous acid*).

If allowed to remain at high pressures in a sealed tube it becomes bluish green, and drops of blue liquid appear, first noticed at about 28 atms. If hydrochloric acid be also present, NOCl is formed, the change being probably represented by

$$6NO=2N_2O_3+N_2$$
$$N_2O_3+2HCl=2NOCl+H_2O$$

(Briner and Wroczynski, Compt. rend. 1909, 149, 1372).

It is absorbed by a number of acids and salts, forming compounds of whose constitution little is known, which break down again on dilution with water, or gently heating.

H_2SO_4 in presence of oxygen yields

$$NO{\cdot}OSO_3H$$

(Lunge, Ber. 1885, 18, 1384).

It reacts with nitric acid (*v.* Saposhnikoff, J. Russ. Phys. Chem. Soc. 1901, 33, 506, and under HNO_3) and is absorbed by phosphoric acid (Reinsch, J. pr. Chem. 1843, 28, 385), arsenic, and some organic acids, and by many halides, such as those of B, Si, Bi, Fe, Cu (for example $BiCl_3{\cdot}NO$; $2FeCl_3{\cdot}NO$) (Besson, Compt. rend. 1889, 108, 1012; Thomas, Ann. Chim. 1898, [vii.] 13, 145). $FeSO_4$ gives the compound $FeSO_4{\cdot}NO$ (Manchot and Zechentmayer, Annalen, 1906, 350, 368; *v.* Hûfner, Zeitsch. physikal. Chem. 1907, 59, 416; Asher, *ibid.* 1908, 62, 622) which has been isolated in red leaflets (Manchot and Huttner, Annalen, 1910, 372, 153; Manchot, Ber. 1914, 47, 1601; Bellucci, Gazz. chim. ital. 1914, ii. 384). Conductivity of NO in $FeSO_4$ solutions (Zimmermann, Monatsh. 1905, 26, 1277). It combines with Ni, Co, and Mn sulphates (*v.* Hûfner, *l.c.*; Asher, *l.c.*)

$Fe_2(SO_4)_3{\cdot}NO$ is formed from ferric sulphate in 90 p.c. H_2SO_4 solution (Manchot, Zeitsch. physikal. Chem. 1910, 372, 179).

The violet coloration produced by NO in solutions of $CuSO_4$ in concentrated H_2SO_4 is due to the formation of an easily dissociated compound $CuSO_4{\cdot}NO$ (Manchot, Annalen, 1900, 375, 308).

A number of other iron-nitric oxide-sulphur derivatives of uncertain constitutions are described by Hofmann and Wrede (Zeitsch. anorg. Chem. 1896, 11, 288, and previous references), Marie and Marquis (Compt. rend. 1896, 122, 137), Bellucci and Venditori (Atti R. Accad. Lincei, 1905, [v.] 14, i. 98), Manchot (Zeitsch. angew. Chem. 1911, 24, 18) and Raschig (*ibid.* 160).

Complex cyanogen compounds are described by Miolatti (Zeitsch. anorg. Chem. 1900, 25, 318); complex nitrates and chlorides of the type $CO(NH_3)_5(NO)X_2$ by Sand and Singer (Annalen, 1903, 329, 190), and other complex amines containing NO by Werner.

Nitrogen trioxide, *Nitrous anhydride.* When nitric oxide and nitrogen peroxide are mixed, or when half the corresponding atomic proportion of oxygen is added to nitric oxide, a gas is obtained which appears to be a mixture of N_4O_6 molecules with N_2O_4, NO_2, and NO molecules in relative amount dependent on the temperature and extent of drying. At low temperatures the substance consists mainly of N_4O_6 molecules, and as it vaporises it is dissociated thus—

$$N_4O_6 \rightleftarrows N_2O_3+NO_2+NO$$

N_4O_6 molecules in the liquid state are blue, whilst in the gaseous state both N_4O_6 and N_2O_3 are colourless or nearly so. On gently warming the blue liquid becomes green, owing probably to the yellow NO_2 molecules produced by the dissociation giving with the blue N_4O_6 molecules a green mixture (B. M. Jones, Chem. Soc. Trans. 1914, 105, 2310), *cf.* Wourtzel, Compt. rend. 1920, 109.

Preparation.—(1) By reduction of nitric acid of suitable concentration by a reducing agent, usually starch or As_4O_6. According to Lunge (Ber. 1878, 11, 1229), acid of sp.gr. 1·20 gives NO, acid of sp.gr. 1·35 N_2O_3, and sp.gr. 1·5 practically all NO_2. As, however, the product varies with the concentration, obviously a pure compound cannot be obtained, as the concentration is changing throughout the experiment, and Ramsay and Cundall (Chem. Soc. Trans. 1885, 187) recommend acid of initial concentration 1·5 as the most suitable. The arsenious oxide and nitric acid are carefully heated on the water-bath in a large retort or distilling flask. The action is apt to become very violent. The gas is dried over solid calcium chloride and liquefied by ice and salt. If N_2O_4 is in excess a bluish-green liquid results, which, on volatilising in a current of NO and recondensing, yields an indigo blue liquid at −10°. Its ready dissociation into NO and N_2O_4, the former of which is only liquid at −165°, the latter easily condensable, renders the removal of the last traces of N_2O_4 exceedingly difficult.

(2) By oxidation of nitric oxide with oxygen. At temperatures below −100° the product from any proportions of these gases is always N_2O_3 (*v.* under *Nitric oxide*).

(3) By oxidation of liquid nitrogen by passing electric discharges through liquid air. So formed it remains suspended in the liquid air as a flocculent green substance, strongly resembling precipitated chromic hydroxide, but on evaporation of the excess of air is left as a slightly blue amorphous powder, which melts at −111°, and then assumes a deep blue colour which persists after resolidification in liquid air (Helbig, Atti R. Accad. Lincei. 1903, [v.] 12, 1, 166; Fischer and Braemar, Ber. 1906, 39, 940). According to Scarpa (Gazz. chim. ital. 1907, 37, ii. 185), NO is formed in the region of the arc, and in the boiling air combines further with oxygen, giving N_2O_3, which under favourable conditions may be complete, since N_2O_4 is solid at temperatures lower than the critical dissociation temperature. The best form of apparatus is described.

(4) By reduction of N_2O_4 by NO (Péligot, Ann. Chim. 1841, [iii.] 2, 58; Porschnew, Zeitsch. anorg. Chem 1894, 7, 214). On saturating liquid N_2O_4 with NO and subsequently cooling dark blue crystals of N_4O_6 separate, m.p. −193°, no other compound being formed. The eutectic mixture (63·6 N_2O_4,

36·4 NO), melts at −112° (Wittorff, J. Russ. Phys. Chem. Soc. 1904, 36, 857).

(5) By the action of 5N and 6N nitric acid upon copper. The gaseous product consists almost entirely of nitrogen trioxide. With stronger acid nitrogen peroxide is formed in amount depending upon the strength of the acid (Bagster, Chem. Soc. Trans. 1921, 119, 82).

N_2O_3 is also produced by action of water on lead chamber crystals, and on nitrogen peroxide.

Properties.—Nitrogen trioxide, at ordinary temperatures, gives a brown gas which has a density corresponding to a mixture of NO and NO_2, allowing for polymerisation of the latter (Ramsay and Cundall, Chem. Soc. Trans. 1890, 37, 590; Porschnew, *l.c.*), borne out by the fact that the spectra of NO_2 and gaseous N_2O_3 are identical (Moser, Wied. Ann. 1877, 2, 139), while the blue liquid has no definite b.p. At −21°, however, its composition is very closely N_4O_6 (Francesconi and Sciacca, Gazz. chim. ital. 1904, 34, 1, 447). From the vapour pressure curves between −80° and 35° the b.p. of pure nitrogen trioxide would appear to be −27°/760 mm. By prolonged drying over phosphoric oxide, H. B. Baker and M. Baker found that its temperature could be raised to 43° before any sign of ebullition could be detected (Chem. Soc. Trans. 1912, 2339). M.p. −103° (Wittorff), −111° (Helbig); sp.gr. at 0° 1·4490 (Geuther, Annalen, 1888, 245, 96).

Pure nitrogen trioxide can exist only at very low temperatures in the solid state, or in the liquid state under pressure of nitric oxide. At temperatures above −100° it dissociates. It is not possible to distil it in a vacuum because of the immediate formation of an atmosphere of nitric oxide at temperatures at which distillation is possible (Baume and Robert, Compt. rend. 1919, 169, 968).

The discovery that dissociation of ammonium chloride and other substances does not take place in complete absence of moisture led to a similar investigation of nitrogen trioxide (Baker and Baker, Chem. Soc. Trans. 1907, 1862). Bulbs containing known weights of the carefully prepared and dried liquid were broken in a Lunge nitrometer over dry mercury (which is practically unaffected), and the densities so found varied from 43·2 to 48·6, that of undissociated N_2O_3 being 38. On admitting concentrated H_2SO_4 absorption took place so rapidly that the impact of the mercury endangered the tube, whereas a mixture of NO and N_2O_4 is only comparatively slowly absorbed. Further determinations with a special V. Meyer apparatus (*ibid.* 1900, 647) varied from 38·1 to 62·2, the samples being taken from several preparations which had been condensed at different temperatures and dried for varying lengths of time, and containing varying proportions of the polymeric N_4O_6, which, however, was not obtained in the pure condition.

In the hope that in solution at low temperatures the higher polymeride would be present in greater amount, molecular weight determinations were made in benzene solution, but the values obtained were 83, 83·2, and 95, showing this not to be the case. Nitrogen trioxide is without action on benzene.

As usually prepared it mixes with water, giving a blue-green liquid which above 0°, by further concentration, evolves NO, and on dilution gives nitrous acid; but according to Baker it is practically insoluble in water and sinks, forming NO and N_2O_4, the latter dissolving in the water.

With concentrated H_2SO_4, *nitrosylsulphuric acid* (*q.v.*) is formed.

Oxygen is without action below −110°. Above −100° it is converted into N_2O_4 (*v.* under NO). As an oxidising agent on metals it behaves as a mixture of NO and NO_2, NO being formed at low temperatures, and N_2 at higher temperatures. Like N_2O_4 it is absorbed by alkalis, but more rapidly, and it is supposed that it is the N_2O_3 in the equilibrium

$$NO+NO_2 \rightleftarrows N_2O_3$$

which is absorbed (*cf.* Le Blanc, Zeitsch. Elektrochem. 1906, 12, 544). This is borne out by the fact that liquid N_4O_6 at −22° is instantly absorbed by NaOH, whereas liquid N_2O_4 reacts only slowly (Foerster and Blich, Zeitsch. angew. Chem. 1910, 23, 2017). Dry nitrogen trioxide is quantitatively absorbed by dry potassium hydroxide (Klinger, Zeitsch. angew. Chem. 1914, 27, 7).

Its solution in carbon tetrachloride reacts with one of SO_3 precipitating *sulphonitrous anhydride* $(SO_3)_5(N_2O_3)_2$ in needles, m.p. 190°–200°; b.p. 302°–305°/728 mm. Hence Provostaye's *nitrosyl sulphate* (Ann. Chim. 1840, [ii.] 73, 362), m.p. 217°–230°; b.p. 360°, is therefore of greater complexity than $(SO_3)_2N_2O_3$, probably $(SO_3)_8(N_2O_3)_3$. The *tetrasulphate* is also known (Pictet and Karl, Bull. Soc. chim. 1908, [iv.] 3, 1114).

Nitrosyl perchlorate $NO{\cdot}OClO_3{\cdot}H_2O$ separates in leaflets when N_2O_3 is passed into concentrated perchloric acid (Hofmann and Ledtwitz, Ber. 1909, 42, 2031). With unsaturated carbon compounds it forms additive compounds.

Nitrogen peroxide, or **tetroxide** ('hyponitric acid'). This oxide is only capable of existing as NO_2 in a pure condition within narrow limits of temperature. At low temperatures the polymerised product N_2O_4 is the stable form, which dissociates on rise of temperature into NO_2, but this in turn is easily dissociated on further rise of temperature into NO and oxygen. For its decomposition under the influence of the electrical glow, *see* Zenneck and Strasser, Zeitsch. physikal. Chem. 1911, 12, 1201.

Preparation.—It is produced by oxidation of nitric oxide with oxygen, as first shown by Gay Lussac, and thus results on oxidation of nitrogen with excess of oxygen under ordinary conditions. NO and O_2 in the proportion 2 : 1, dried and well mixed by passing through a tube filled with glass or porcelain fragments, condense at −20° to a colourless crystalline mass of N_2O_4 (Dulong, Ann. Chim. 1816, [ii.] 2, 317; Péligot, *ibid.* 1841, [iii.] 2, 58). Similarly the gas resulting from the action of concentrated nitric acid on arsenious oxide is converted by excess of oxygen into N_2O_4.

Mandl and Russ (Zeitsch. angew. Chem. 1908, 21, 486) state that the rate and extent of union of NO and O_2 is affected by the character of the oxygen; for example, electrolytic oxygen is more active after passing over heated palladium, and ozonisation retards the action.

According to Holwech (*ibid.* 2131), however, this is not the case, union being practically complete in each instance, and the velocity of reaction the same with oxygen from all sources.

A good yield of NO_2 is said to be obtained by passing air and steam through a thin-walled porous porcelain tube at 1600°, the diffusion of the hydrogen formed being increased by raising the inside pressure and lowering that outside the tube (Westdeutsche Thomasphosphatwerke, D. R. P. 182297).

It is also obtained by passing nitric acid vapour through a hot tube, and by heating metallic nitrates,

$$Pb(NO_3)_2 = PbO + O + 2NO_2$$

Those of the alkalis evolve NO_2 when electrolysed in the fused condition (Bogorodski, J. Russ. Phys. Chem. Soc. 1905, 37, 703). It is formed by union of N_2O_3 and N_2O_5. Also by treating with fuming sulphuric acid a homogeneous mixture of alkali nitrate and nitrite, made by fusing the salts together or pouring the fused mixture into carbon tetrachloride.

$$NaNO_2 + NaNO_3 + H_2S_2O_7 = 2NaHSO_4 + 2NO_2$$

Sufficient $NaHSO_4$ from a previous preparation is added to fix any free SO_3 present—

$$2NaHSO_4 + SO_3 = Na_2S_2O_7 + H_2SO_4$$

(Winans, D. R. P. 193696).

It is evolved on warming chamber crystals with KNO_3, thus :

$$NO_2 \cdot SO_3H + KNO_3 = 2NO_2 + KHSO_4$$

and by the action of nitric acid on nitrous acid or a nitrite—

$$HNO_3 + R \cdot NO_2 = R \cdot OH + 2N_2O_2$$

(Girard and Pabst, Bull. Soc chim. 1878, [ii.] 30, 531).

Properties.—At ordinary temperatures an orange-coloured corrosive gas of peculiar and unpleasant odour. At higher temperatures it becomes much darker in colour, turning lighter again on further rise, and finally colourless when dissociation into NO and oxygen is complete. It condenses to an orange-yellow liquid, b.p. 25°–26° (Hasenbach; Bruni and Berti, Atti R. Accad. Lincei, 1900, [v.] 9, i. 321); 21·97° (Thorpe and Rodger, Phil. Trans. 1804, 451); 21·2° (Scheffer and Treub, Proc. K. Akad. Wentensch Amsterdam, 1911, 14, 536). For the influence of prolonged contact with phosphoric oxide in modifying the b.p. of nitrogen peroxide, *see* H. B. Baker and M. Baker (*l.c.*). At 10° it is pale yellow, and when solid colourless. M.p. $-10 \cdot 1°$ (Ramsay, Zeitsch. physikal. Chem. 1890, 5, 221), $-10 \cdot 95°$ (Bruni and Berti, *l.c.*), $-10 \cdot 8°$ (Scheffer and Treub (*l.c.*), $-10 \cdot 5°$ (Egerton). Critical temperature 171·2°, 158·2° (Scheffer and Treub); critical pressure 100 ± 2 atmospheres.

In the solid state it probably exists entirely as N_2O_4, and almost entirely so in the liquid state, though not ascertained by experiment. In the gaseous state and in solution, however, its behaviour is accurately known from its vapour density measurements, which are in accord with the conclusions drawn from other physical properties, such as absorption of light, conductivity for heat, and specific heat. The vapour pressure of nitrogen peroxide has been studied by Guye (J. Chim. Phys 1910, 8, 473), Scheffer and Treub (Proc. K. Akad. Wetensch. Amsterdam, 1911, 14, 536), Russ and Eberwein (Zeitsch. physikal. Chem. 1913, 82, 217), and Egerton (Chem. Soc. Trans. 1914, 105, 647). The following table given by Egerton shows the vapour pressure of solid nitrogen peroxide for every 10° below −30° down to −100°, calc. by $\log p = 14 \cdot 9166 + \theta(0 \cdot 0604)$:—

Temp.	Press in mm.	Temp.	Press. in mm.
−30°	39·24	−70°	0·151
−40°	9·77	−80°	0·036
−50°	2·44	−90°	0·0093
−60°	0·605	−100°	0·0023

According to Scheffer and Treub the vapour pressures at higher temperatures are as follows :—

°	mm.	°	mm
− 36·0	18	7·7	293
− 23·0 (solid)	53	15·0	565
23·0	70	21·45	770
− 10·0	146	27·4	1007
− 6·9	180	39·0	1668
− 0·6	256	43·2	1982

The liquid is not polymerised further than N_2O_4 nor is the gas, as shown by its molecular weight in acetic acid (Ramsay and Shields, *ibid.* 1893, 12, 433; Ramsay, Chem. Soc. Trans. 1888, 53, 621).

Its further dissociation into nitric oxide and oxygen is accurately known from its density.

	−5°	−2°	0°	5°	10°	15°
Sp.gr	1·5035	1·5020	1·4935	1·4880	1·4770	1·4740

(Geuther, Annalen, 1888, 245, 96). At 0° 1·4903; at 21·6° 1·4396 (Thorpe, Chem. Soc. Trans. 1880, 37, 224); *cf.* Bousfield, Chem. Soc. Trans. 1919, 47.

Thorpe finds the expansion of liquid N_2O_4 to be very regular, 1 vol. at 0° becoming at

5°	10°	15°	20°
1·00789	1·01573	1·02370	1·03196

Pascal and Garnier (Bull. Soc. chim. 1919, [iv.] 25. 309), find that the density of nitrogen peroxide between 0°–21·5° may be represented by the equation $Dt_4 = 1 \cdot 490 - 0 \cdot 00215t$ The vapour densities found by various observers have been collected by Schreber (Zeitsch. physikal. Chem. 1897, 24, 651), and the dissociation constants calculated. The following values of $K = [N_2O_4]^{\frac{1}{2}}/[NO_2]$ are given—

$t°$	K
0·0	8·060
18·3	3·710
49·9	1·116
73·6	0·544
99·8	0·273

At 64° one-half of the N_2O_4 mols are dissociated, and at 150° they are wholly dissociated (*v.* also Bodenstein and Katayama, Zeitsch. Elektrochem 1909, 15, 244). Above 150° decomposition into NO and oxygen takes place, and at 620° is practically complete. At 184°, 5 p.c. is dissociated, and at 494° 56·5 p.c (Richardson, Chem Soc. Trans. 1887, 51, 397). Sp.ht. of liquid 0·477° (Ramsay, Zeitsch. physikal. Chem. 1890, 5, 221).

Apparently anomalous values, obtained by Berthelot and Ogier (Ann. Chim. 1883, 30,

382) for the sp.ht. of the gas, are explainable by its dissociation (Swart, Zeitsch. physikal. Chem. 1891, 7, 120).

Heat of formation $2N+4O=N_2O_4$ −3900 cal. (Thomsen) (9 p.c. NO_2, 91 p.c. N_2O_4). Heat of dissociation about −13,000 cal., and calculated heat of formation of undissociated N_2O_4 −2650, and of NO_2 −8125 cal. Heat of formation of liquid −2200 and −2500 cal. (for $NO_2=46$ gr.) (Berthelot, Ann. Chim. 1875, [v.] 6, 145); heat of vaporisation at 180° −4300 cal. Latent heat of fusion −32·2 to −37·2 cal.; calculated from freezing-point lowering, −33·7 (Ramsay, *l.c.*).

The heat conductivity values also reveal its dissociation (Feliciani, Chem. Zentr. 1905, i. 331). At 150°, the conductivity of NO_2 is 0·0033.

Refraction equivalent of liquid 11·8, dispersion equivalent 0·82 (Gladstone, Chem. News, 1887, 55, 300). Refractive index of vapour at 36°, 1·000503 (Dulong; *v.* Zeitsch. physikal. Chem. 1901, 36, 332; *cf.* C. and M. Cuthbertson, Proc. Roy. Soc. 1913, A, 89, 361). For the spectra of nitrogen peroxide, *v.* Bell (Amer. Chem. J. 1885, 7, 32). The vapour does not conduct electricity, and the liquid only slightly.

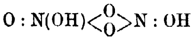
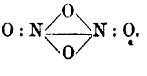
Dielectric constant (*v.* Badeker, Zeitsch. physikal. Chem. 1901, 36, 305).

Chemical properties.—It is reduced to ammonia if passed with hydrogen over platinum black (Kuhlmann, Annalen, 1839, 29, 272), or over reduced nickel or copper (Sabatier and Senderens, Compt. rend. 1902, 135, 278). Carbon, sulphur and phosphorus burn in the gas, carbon monoxide burns to CO_2, and hydrogen sulphide to sulphur, with formation of NO.

Potassium burns with a red flame, and sodium, though not igniting, decomposes the gas at the ordinary temperature, while many metals and lower oxides are oxidised on heating to 500°, and some metals form additive compounds ('nitro metals') with the liquid $N_2O_4(Cu_2NO_2, Ni_4NO_2)$ similar to the carbonyl compounds (Sabatier and Senderens, Ann. Chim. 1896, [vii.] 7, 348). Other metals, such as K, Na, Hg, Pb, form the nitrate with production of NO. It also forms additive compounds with many metallic salts ($FeCl_3{\cdot}NO_2$, $SnCl_4{\cdot}NO_2$, &c.) (Thomas, *ibid.* 1898, [vii.] 13, 145) and with unsaturated organic compounds (nitrosates).

With water N_2O_4 exhibits its mixed anhydride character. With small quantities of water, however, the reaction

$$2N_2O_4+H_2O=N_2O_3+2HNO_3$$

takes place at low temperatures, two layers being formed, the lower, deep blue N_2O_3. Further dilution converts the nitrous anhydride to nitrous acid, which on rise of temperature is decomposed with evolution of NO (Schönbein, Pogg. Ann. 1848, 73, 326). *Cf.* Oddo (Gazz. chim ital. 1915, 45, i. 413) who finds that nitrogen peroxide tends to form a hydrate to which he gives the name of *nitrosic acid* and the constituted  $O:N(OH)\langle{}^{O}_{O}\rangle N:OH$, and to nitrogen peroxide the structure  O : N<O, O, O>N : O.

With aqueous alkalis, a mixture of nitrite and nitrate is formed (*v.* also under N_2O_3). Metallic oxides under pressure form the nitrate only, evolving NO. BaO, however, according to Dulong, forms a mixture of nitrite and nitrate at 200° (Annalen, 1862, 122, 18).

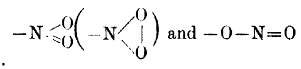
Liquid ammonia reacts explosively with solid N_2O_4 at −80°, but a current of gaseous NH_3 led over the solid at −20° reacts less vigorously, and the products are N_2, NO, H_2O, NH_4NO_3 and a trace of NH_4NO_2 (Besson and Rosset, Compt. rend. 1906, 142, 633). Dry oxygen does not oxidise it, but ozone converts it to the pentoxide. In presence of water, oxygen and oxidising agents convert it into nitric acid. It is absorbed by dilute and concentrated HNO_3 (*v.* Weber, Pogg. Ann. 1867, 130, 277; Lunge, Ber 1879, 12, 1058; Bousfield, Chem. Soc. Trans. 1919, 45). The density of nitric acid shows a marked increase with the addition of nitrogen peroxide (*cf.* Lunge and Marchlewsky, Zeitsch. angew. Chem. 1912, 10), reaching a maximum when the mixture contains about 42·5 p.c. by weight of the peroxide, corresponding to $N_2O_5,N_2O_4{\cdot}H_2O$, stable at −48·5°, above which temperature it dissociates (Pascal and Garnier, *l.c.*). With SO_2 and SO_3 it gives various substances of not very clearly defined character (Weber, *l.c.*; Hasenbach, J. pr. Chem. 1871, [ii.] 4, 4; Friedburg, Chem. News, 1883, 47, 52). With sulphuric acid it forms *nitrosyl-sulphuric* and *nitric acids*,

$$H_2SO_4+N_2O_4=NO_2{\cdot}SO_3H+HNO_3$$

(Lunge, Ber. 12, 357).

It has been used as a solvent for cryoscopic measurements. Molecular raising of b.p. 13·7°, molecular lowering of freezing-point 41° (Ramsay, Zeitsch. physikal. Chem. 1890, 5, 221; Frankland and Farmer, Chem. Soc. Trans. 1901, 79, 1356; Bruni and Berti, Gazz. chim. ital. 1900, 30, ii. 151). The liquid has been used in explosives (Settlick, Chem. Zentr. 1888, 461).

Constitution.—The formula of the dioxide may be written—



$$-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown\!\!= O}\left(-N\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}\right) \text{ and } -O-N=O$$

and that of the tetroxide—

$O_2=N-N=O_2$, $O_2=N-O-N=O$, $O=N-O-N=O$

The reaction with water favours the second of these. Piloty and Schwerin (Ber. 1901, 34, 1884 and 2354) suggest $O=N=O$ as the formula for the dioxide; but Divers (Chem. Soc. Trans. 1904, 110) prefers the formula $O-N=O$ for the dioxide, and for N_2O_4 advances reasons in favour of the formula $(NO)_2O_2$, 'di-nitric peroxide.'

Pure nitrogen peroxide does not react with cold aromatic hydrocarbons. With benzene at 80° the main products are 1.3.5-trinitrobenzene and picric acid. Nitrobenzene is indifferent at 80°. Phenol dissolved in a cold mixture of benzene and light petroleum is readily nitrated to *o*- and *p*-nitrophenol. *o*-Cresol gives *o*- and *p*-nitro-*o*-cresol; *m*-cresol yields *o*- and *p*-nitro-*m*-cresol, whilst the *p*- compound gives *o*-nitro-*p*-cresol and *o*-dinitro-*p*-cresol. 1.3.4 *m*-xylenol is converted into the corresponding 5-nitro-compound.

α Naphthol gives a mixture of 2-nitro-α-naphthol and 2 4-dinitro-α-naphthol. Acetanilide in ethereal solution is transformed into benzene-diazonium nitrate. Diphenylamine in ethereal solution yields diphenylnitrosamine; in benzene solution it gives *p*-nitrodiphenylnitrosamine (Wieland, Ber. 1921, 54, 1776; J. Soc Chem. Ind. 1921, 40, 763, A). A consideration of these reactions leads to the formula $O_2N{\cdot}NO_2$ as the most probable constitution of nitrogen peroxide, which is also in accord with its other reactions and its dissociability; its decomposition by alkali is then analogous to that of other symmetrically-paired atoms or radicles, *e.g.* cyanogen to cyanide and cyanate, chlorine to chloride and hypochlorite.

iso-Nitrogen tetroxide.—According to Raschig (Chem. Zeit 1907, 31, 359), the red vapours formed from nitric oxide and air are of different composition from that usually accepted, the first product being *iso*-nitrogen tetroxide (*a*) distinguished from the ordinary tetroxide (*b*) by its reaction with sodium hydroxide—

$$(a)\ N_2O_4+2NaOH=2NaNO_2+H_2O+O$$
$$(b)\ N_2O_4+2NaOH=NaNO_2+NaNO_3+H_2O$$

With larger excess of oxygen the *iso-pentoxide* and a *hexoxide* and *heptoxide* are said to be formed—

$$N_2O_5+2NaOH=NaNO_2+NaNO_3+H_2O+O$$
$$N_2O_6+2NaOH=2NaNO_2+H_2O+3O$$
$$N_2O_7+2NaOH=NaNO_2+NaNO_3+H_2O+3O$$

(*cf.* Muller, Zeitsch. anorg. Chem. 1912, 76, 324; *ibid.* 1914, 86, 230; Raschig, *ibid.* 1913, 84, 115).

According to Muller the green substance, assumed by Raschig to be NO_3, is a mixture. The colour may be exactly imitated by dipping a test-tube containing liquid air in liquid nitrogen trioxide, and after a frozen layer has been formed, in liquid nitrogen tetroxide. The two layers of blue and yellow give a green, which is exactly similar to that of the supposed hexoxide.

Nitrogen pentoxide, *nitric anhydride* N_2O_5, may be prepared as follows:—

(1) By oxidation of nitrogen peroxide with ozone (Helbig, Atti R. Accad. Lincei, 1903, [v.] 12, i. 211; Zeitsch. Elektrochem. 1906, 12, 550).

(2) As first prepared by Deville (Ann. Chim. 1849, [iii.] 28, 241) by action of dry chlorine on silver nitrate warmed to 50°–60°.

$$4AgNO_3+2Cl_2=4AgCl+O_2+2N_2O_5$$

the gaseous product being condensed in a freezing mixture.

(3) Most conveniently, as first obtained by Weber, by dehydration of pure nitric acid with phosphorus pentoxide, with constant cooling (Meyer, Ber. 1889, 22, 23).

The syrupy liquid produced is poured into a dry retort and distilled into a receiver surrounded by a freezing mixture. The orange-red distillate separates into two layers, the upper of which is poured into a separating funnel and cooled in ice. The crystals formed are drained, again melted and crystallised and drained from the mother liquor

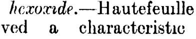
The operation is facilitated by performing the operation in a current of ozonised oxygen, which prevents decomposition into oxygen and lower oxides of nitrogen; to remove the last traces of moisture the gases should be passed through a long tube containing phosphorus pentoxide. The nitrogen pentoxide is almost completely condensed at −80° (Russ and Pokorny, Monatsh. Chem. 1913, 34, 1051; Daniels and Bright, J. Amer. Chem. Soc 1920, 42, 1131).

After recrystallisation it is obtained in white glistening rhombic crystals, sp.gr. 1·63, m p. 29·5° (Berthelot, Bull. Soc. chim. 1874, [ii] 21, 53) It boils with decomposition into N_2O_4 and oxygen at about 45°. It darkens in colour on rise of temperature, the crystals becoming yellow some time before melting, at which point it is orange coloured, further turning dark-brown as the temperature rises. The vapour pressure of nitrogen pentoxide is given by the formula—

$$\log P_{mm}=1244/T+34{\cdot}1\log T-85{\cdot}929$$

(Daniels and Bright, J. Amer. Chem Soc. 1920, 42, 1131). Calculated molecular heat of fusion −8280 cal., and heat of evaporation −4840 cal. Heat of formation of solid N_2O_5 13,100 cal. (Berthelot, Ann. Chim Phys 1875, [v.] 6, 202). Hence heat of formation of gaseous N_2O_5 is practically nil. Heat of sublimation for various absolute temperatures: 263°, 12,360 cal.; 273°, 12,760; 283°, 13,360; 293° 14,140 (Daniels and Bright, *l.c.*). Heat evolved with one molecule of water, 2300 cal Heat of solution in excess of water 16,200 cal. (Berthelot, *l.c.*).

N_2O_5 dissolves in water giving nitric acid. It has no action on carbon or metals. It is useful as a nitrating agent. For this purpose, Gibson (Proc. Roy. Soc. Edin. 1908, 28, 705) gives details for making large quantities. It dissolves in freshly distilled and fused sulphur trioxide, giving a practically pure product in almost theoretical yield, b.p. 218°–220°; m.p. 124°–128°, which is also obtained as a crystalline precipitate on mixing carbon tetrachloride solutions. Its formula is $(SO_3)_4{\cdot}N_2O_5$, and its probable constitution—



$$O<\begin{matrix}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO_2\\SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO_2\end{matrix}$$

(Pictet and Karl, Compt. rend. 1907, 145, 238).

Nitrogen hexoxide.—Hautefeuille and Chappuis observed a characteristic absorption spectrum during the passage of a silent electric discharge in air (Compt. rend. 92, 80; 94, 946, 1306). Warburg and Leithäuser (Sitzungsber. Akad. Wiss. Berlin, 1907, 229) observed the same from ozone and N_2O_5 at 0°–18°. It is suggested that it is due to a higher oxide, probably N_2O_6. (*cf.* Müller, Zeitsch. anorg. Chem. 1912, 76, 324).

Nitrous acid HNO_2. Nitrous anhydride dissolves in excess of ice-cold water with production of this acid. The solution, however, is extremely unstable (*cf.* Knox and Reid, J. Soc. Chem. Ind. 1919, 38, 105, T), but its metallic and ethereal salts are comparatively stable.

Nitrites are found to some extent in nature, and occur in the sap of certain plants (Mazé, Compt. rend. 1912, 155, 781; Bach, Biochem. Zeitsch. 1913, 52, 418; Klein, Bied. Zentr.

1915, 44, 162). Their universal presence in air has been shown by Schönbein (Chem. News, 1862, 241), Warington (Chem. Soc. Trans. 1881, 220), and Hayhurst and Pring (*v.* under NITROGEN).

All nitrites are soluble in water, and the majority dissolve in alcohol.

Preparation.—Alkali and alkaline earth hydroxides and carbonates absorb N_2O_4 and N_2O_3, in the first case, giving a mixture of nitrite and nitrate, and in the second case, if NO be present in slight excess, practically pure nitrite (Divers, Chem. Soc. Trans. 1899, 75, 85). The acid may be obtained in solution by the action of dilute sulphuric acid upon a solution of barium nitrite. On the commercial scale, the nitrous fumes electrically produced from the air are kept at 300° until absorbed, whereby oxidation of the NO only proceeds as far as N_2O_3, and on absorption (in strong nitrite solutions, which have low vapour tensions) pure nitrite is produced (Badische Anilin u. Soda Fabrik, D. R. P. 188188).

For the formation of ammonium nitrite, *see* Rây, Chem. Soc. Trans. 1909, 95, 345; Neogi and Adhicary, *ibid.* 1911, 99, 116.

Nitrites are obtained by reduction of nitrates, and also by oxidation of nitrogen compounds richer in hydrogen.

For the formation of nitrites from nitrates in aqueous solution under the action of sunlight, *see* Moore, Proc. Roy. Soc. 1917. For their photochemical assimilation, *see* Baudisch and Mayer, Zeitsch. physiol. Chem. 1914, 89, 175.

Many nitrates are reduced to nitrites by fusing with lead, copper, carbon (Fischer, Pogg. Ann. 1848, 74, 115), sulphites (Etard, Bull. Soc. chim. 1877, [ii.] 27, 434), sulphides (Roy, Compt. rend. 1889, 108, 1251), and in solution by reduction with Na, K, Ca and other metals (Schönbein, J. pr. Chem. 1868, 105, 206), and further by electrolytic reduction, the conditions for which have been worked out by Muller and Weber (Zeitsch. Elektrochem. 1903, 9, 955, 978) and Muller and Spitzer (*ibid.* 1905, 11, 917). Silver is found to be the best cathode, reduction to nitrite being almost complete before further reduction to ammonia takes place. Using a copper anode the yield is almost quantitative.

Nitrites are also produced by oxidation of ammonia with hydrogen peroxide (Weith and Weber, Ber. 1874, 7, 1745; Hoppe-Seyler, *ibid.* 1883, 16, 1916).

According to Oswald (Ann. Chim. 1914, [ix.] 1, 32), the only practical method for the preparation of pure nitrites of the alkali and alkaline-earth metals is by double decomposition of silver nitrite with the chlorides of those metals.

Schönbein has shown that copper is oxidised when immersed in aqueous ammonia in contact with air, whilst the ammonia is at the same time oxidised to nitrite, and Traube and Biltz (Ber. 1904, 37, 3130; 1906, 39, 166) have studied the electrolytic oxidation of aqueous NaOH containing ammonia, in presence of copper hydroxide as catalyser. With a current strength of 5–15 amperes and platinum or iron electrodes, practically the whole of the anode oxygen is used up in converting the ammonia present into nitrite. The final product is nitrate.

Properties.—Though very unstable in solution it is chemically a fairly strong acid, about 20 times as strong as acetic acid. It is slowly displaced from solutions of its salts by carbon dioxide (Moore, J. Amer. Chem. Soc. 1904, 26, 959).

The velocity constant of decomposition =0·00014 at 0°, 0·00022 at 21°, and 0·00057 at 40° (Rây, Dey and Ghosh, Chem. Soc. Trans. 1917, 413).

Conductivities at dilutions of 512, 1024, and 1536, are 150·7, 189, and 217·0 respectively (Schumann, Ber. 1900, 33, 527). Calculated velocity of nitrite ion 64·5 (Pick finds 63 from $AgNO_2$, and Vogel (Zeitsch. anorg. Chem. 1903, 35, 385) 61·7 from $Ba(NO_2)_2$), and dissociation constant 0·00045 at $0^\circ = 6 + 10^4$ (Rây, Dey and Ghosh); Bauer (Zeitsch. physikal Chem. 1902, 41, 681) finds 0·00064.

Heat of neutralisation (with baryta) 10,600 cal. (with ammonia) 9100 cal. (Berthelot, Ann. Chim. 1875, [v.] 6, 145).

Heat of formation

$$N + O_2 + H + Aq = HNO_2 + 30{,}770 \text{ cal.}$$

The aqueous solution on warming evolves NO leaving nitric acid

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

this decomposition proceeding in the cold in presence of rough surfaces (sand, glass fragments, &c.). For the dynamics of the equilibrium, *v.* Saposhnikoff (J. Russ. Phys. Chem. Soc. 1901, 33, 506), Lewis and Edgar (J. Amer. Chem. Soc. 1911, 33, 292), and of the decomposition of silver nitrite, Abegg and Pick (Zeitsch. anorg. Chem. 1906, 51, 1).

The solution of the acid is more stable in presence of nitric oxide under pressure. This fact has been applied to the diazotisation of dinitroaniline, tribromoaniline, and *p*-sulphobenzeneazo-*α*-naphthylamine (Briner and Jonas, Helv. Chim. Acta, 1920, 3, 366).

It is completely oxidised to nitric acid by the usual oxidising agents. Its oxidation by hydrogen peroxide and subsequent precipitation with 'nitron' acetate is recommended by Busch (Ber. 1906, 39, 1401) as a good method of estimation. An excellent precipitant for nitrites is 2 : 4-diamino-6-hydroxypyrimidine sulphate (Halon, Ber. 1917, 50, 705). (For its detection and estimation, *v.* under ANALYSIS.)

It also behaves as an oxidising agent, being itself reduced to NO, $H_2N_2O_4$, N_2O, NH_2OH, or even further to N_2 and NH_3 by reducing agents such as stannous chloride, hydrogen sulphide, sodium amalgam (Divers, Chem. Soc. Trans. 1899, 75, 87), and by electrolytic reduction (Tanatar, Ber. 1896, 29, 1039).

The primary reduction product appears to be the radicle NOM′, which gives hyponitrite by condensation, and hydroxylamine and ammonia by reduction (*v.* under *Hyponitrous acid*).

With hydrazine the following quantitative reaction takes place—

$$N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O$$

There is no evolution of nitrogen as Girard and Saporta (Bull. Soc chim. 1904, [iii.] 31, 905) state (Francke, Ber. 1905, 38, 4102).

Constitution.—The molecular weight from cryoscopic measurements in aqueous solution is in accordance with the formula HNO_2

(Saposhnikoff, J. Russ. Phys. Chem. Soc. 1909, 41, 1704).

In most of its reactions its behaviour indicates the constitution $O{=}N{\cdot}OH$, but it may have the constitution $O_2{\equiv}N{\cdot}H$. The fact that many nitrites readily evolve NO_2 on heating, and give nitroparaffins with alkyl iodides, would suggest the latter to be correct (Divers, Chem. Soc. Trans. 1885, 47, 205; Kieseritzky, Zeitsch. physikal. Chem. 1899, 28, 421; Baudisch, Ber. 1916, 49, 1176). As, however, alkyl nitrite is also produced in yield which varies with the alkyl iodide used, this latter reaction affords no definite clue to its constitution.

Ley, on the other hand, shows that mercurous nitrite exists in solution as an oxy salt (Ber. 1899, 32, 1357), and the reduction of nitrous acid to hyponitrous acid also points to an oxy-structure.

Acid Halides of Nitrous Acid.

Nitrosyl fluoride NOF is prepared by the action of nitrosyl chloride on silver fluoride. A small flask containing NOCl cooled to −5° is attached to one end of a long platinum tube containing the silver fluoride, and kept at 200°–250°, and the NOCl slowly distilled through. The product is condensed in a small platinum flask cooled in liquid air, and on fractionation gives a colourless gas, b.p. −56°, m.p. −134°. In the cold, silicon, boron, red phosphorus, and sodium take fire in the gas, and antimony is at once acted on, the fluoride and nitric oxide being formed Lead, aluminium, bismuth, and copper are slowly attacked, but iodine, sulphur, and carbon do not react even on heating. Brown fumes are produced in moist air and with water, hydrofluoric and nitrous acids being formed. Its analysis and vapour density (1·683 air=1) are in agreement with the formula NOF. It closely resembles *nitryl fluoride* NO_2F (*q v.*) in chemical and physical properties, but differs from it in its behaviour towards water and iodine. It gives additive compounds with arsenic and antimony pentafluorides (Ruff and Stauber, Zeitsch. anorg. Chem. 1905, 47, 190; Ruff, Stauber, and Graf, *ibid.* 1908, 58, 325).

Nitrosyl chloride NOCl is obtained—

(1) By direct union of NO and chlorine (Gay Lussac, Ann. Chim. 1848, [iii.] 93, 203).

The best procedure is to pass a mixture of the dried gases in the proportion of 2 : 1 over finely granulated animal charcoal at 40°–50°, under slight pressure (Francesconi and Bresciani, Atti R. Accad. Lincei, 1903, [v.] 12, 1175). According to Briner and Pylkov (J. Chim. phys. 1912, 10, 640) the charcoal is not really necessary and does not affect the yield.

Its formation at low temperatures has been studied by Boubnoff and Guye (J. Chim. Phys. 1911, 9, 290). After removing excess of NO at −160° to −150°, an excess of chlorine (3·4 p.c.) above that required for the formula NOCl always remains, but is expelled at −80°. According to Trautz, the equation $2NO+Cl_2=2NOCl$ does not satisfactorily explain its formation at all temperatures. Between −72° and 40° the product consists practically of NOCl. At higher temperatures it is mixed with a gas richer in nitric oxide, perhaps $(NO)_2Cl$ or $(NO)_3Cl$, and may be also with a gas richer in chlorine, perhaps $NOCl_2$ (*cf.* Coates and Finney, Chem. Soc. Trans. 1914, 2444; Wourtzel, J. Chim. Phys. 1913, 11, 214). Tilden and others have shown that no higher oxychloride exists, and this is confirmed by the liquidus curve, which, however, denotes the existence of a highly dissociative additive compound, probably $NOCl{\cdot}Cl_2$, at about −109°.

(2) By distillation of *aqua regia.*

(3) By distillation of potassium nitrite with phosphorus pentachloride.

(4) By heating nitrosyl sulphate with sodium chloride.

$$NO_2{\cdot}SO_3H+NaCl=NOCl+NaHSO_4$$

(Tilden, Chem. Soc. Trans. 1874, 630, 852; Girard and Pabst, Bull. Soc. chim. 1878, [ii.] 30, 531).

(5) By action of nitrosamines on hydrochloric acid (Lachmann, Ber. 1900, 33, 1035).

(6) By action of hydrochloric acid on N_2O_4 (Muller, Annalen, 1862, 122, 1), and on N_2O_3 (*v.* Briner and Wroczynski, under *Nitric oxide*).

(7) By action of NO on $FeCl_3$ (Thomas, Compt. rend. 1895, 120, 447).

Nitrosyl chloride is a ruby-red mobile liquid, b.p. −5·6°/751 mm., giving lemon-yellow crystals, m.p. −61° to −60°. Critical temperature 163°–164° (Francesconi and Bresciani, *l.c.*). Vapour density (2·29–2·32 at 10°) is in agreement with the formula NOCl. Sp.gr. of liquid 1·4165 at −12°; 1·4250 at −15°; 1·4330 at −18° (Geuther, Annalen, 1888, 245, 96; *cf.* Briner and Pylkov, J. Chem. phys. 1912, 10, 640).

It is fairly stable towards heat, dissociation being first measurable at 700° (Sudborough and Miller, Chem. News, 1890, 62, 1307).

With water it at once gives nitrous and hydrochloric acids, and with metallic oxides forms the nitrite and chloride of the metal (Sudborough, Chem. Soc. Trans. 1891, 59, 655).

It forms double compounds with many metallic chlorides, some of which decompose on heating, evolving NO

$$CuCl{\cdot}NOCl \rightarrow CuCl_2+NO$$

while others are stable and may be sublimed, *e.g.* —$AuCl_2{\cdot}NOCl$—and with unsaturated organic compounds forms addition products like N_2O_3 and N_2O_4.

With amines nitrogen is evolved and the chloride formed

$$R{\cdot}NH_2+NOCl=RCl+N_2+H_2O$$

(Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431). For its action on mercaptans, *v.* Tasker and Jones (Chem. Soc. Trans. 1909, 1910).

Absorption spectrum (*v.* Magnanini, Zeitsch. physikal. Chem. 1889, 4, 427).

Sulphur trioxide forms *nitrosyl sulphonic chloride* $NO_2{\cdot}SO_2Cl$.

Nitrosyl bromide NOBr is obtained as a dark-brown liquid (1) by direct union of NO and bromine at −7° to −15° (Landolt, Annalen, 1861, 116, 177); (2) by action of NaBr on $NO_2{\cdot}SO_3H$ (Girard and Pabst, *l.c.*; *cf.* Trautz and Dalal, Zeitsch. anorg. Chem. 1920, 110, 1).

It boils at −2° with dissociation, thus differing from the chloride, which it resembles in its chemical properties.

Landolt's *dibromide* $NOBr_2$ and Muir's *tribromide* $NOBr_3$ are mixtures of the monobromide with bromine, according to Frölich (Annalen, 1884, 224, 270); but from an investigation of the fusion-point diagram of the reaction products of bromine and nitric oxide, Trautz and Dalal (*l.c.*) find that the fusion curve shows a eutectic of bromine and nitrosyl tribromide, a maximum at −40° corresponding with $NOBr_3$, a second eutectic of $NOBr_3$ and NOBr at above −55°. Nitrosyl tribromide is a brownish-black, almost opaque liquid, which boils, with decomposition, at 32°, $D_4^{20}=2{\cdot}637$.

The corresponding iodine compound has not been isolated.

REACTION OF NITROUS AND SULPHUROUS ACIDS.

The following equations represent the changes which occur—

(1) $HNO_2+H_2SO_3=[NO{\cdot}SO_3H]$ nitrosulphonic acid (1);

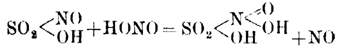
(2) $HNO_2+2H_2SO_3=HO{\cdot}N(SO_3H)_2$ hydroxylamine disulphonic acid (2);

(3) $HNO_2+3H_2SO_3=N(SO_3H)_3$ nitrilo sulphonic acid (3).

The existence of (1) was postulated by Raschig, but has never been isolated, a mixture of equivalent quantities of the two acids giving a very unstable liquid, which by further action of nitrous acid gives—

Nitrosisulphonic acid $HO_2N{\cdot}SO_3H$, also obtained by Sabatier (Compt. rend. 1896, 123, 255) by reduction of nitrosylsulphuric acid.

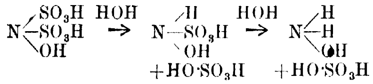
According to Raschig (Zeitsch. angew. Chem. 1905, 18, 1281) its formation and constitution are represented as follows—



$$SO_2{<}\begin{matrix}NO\\OH\end{matrix}+HONO=SO_2{<}\begin{matrix}N{<}\begin{matrix}O\\OH\end{matrix}\\OH\end{matrix}+NO$$

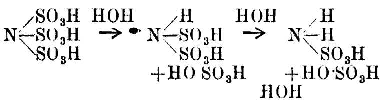
v. also Lunge and Berl (*ibid.* 1906, 19, 808, 857, and 881). The solution of the free acid, and of the copper salt, is blue. The iron salt is red.

Acid hydrolysis of (2) produces successively hydroxylamine sulphonic acid and hydroxylamine—



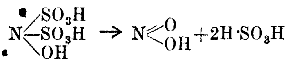
$$N\begin{matrix}{\diagup}SO_3H\\-SO_3H\\{\diagdown}OH\end{matrix}\xrightarrow{HOH}N\begin{matrix}{\diagup}H\\-SO_3H\\{\diagdown}OH\end{matrix}\xrightarrow{HOH}N\begin{matrix}{\diagup}H\\-H\\{\diagdown}OH\end{matrix}$$
$$\qquad\qquad +HO{\cdot}SO_3H \qquad +HO{\cdot}SO_3H$$

Acid hydrolysis of (3) produces successively imino sulphonic acid, amino sulphonic acid, and ammonia—



$$N\begin{matrix}{\diagup}SO_3H\\-SO_3H\\{\diagdown}SO_3H\end{matrix}\xrightarrow{HOH}N\begin{matrix}{\diagup}H\\-SO_3H\\{\diagdown}SO_3H\end{matrix}\xrightarrow{HOH}N\begin{matrix}{\diagup}H\\-H\\{\diagdown}SO_3H\end{matrix}$$
$$\qquad\qquad +HO{\cdot}SO_3H \qquad +HO{\cdot}SO_3H \xrightarrow{HOH} NH_4HSO_4$$

Hydrolysis by alkalis usually regenerates the sulphite and nitrite—



$$N\begin{matrix}{\diagup}SO_3H\\-SO_3H\\{\diagdown}OH\end{matrix}\rightarrow N{<}\begin{matrix}O\\OH\end{matrix}+2H{\cdot}SO_3H$$

For further details, and conditions under which these compounds are formed, *v.* HYDROXYLAMINE

Hyponitrous acid $H_2N_2O_2$. The sodium salt of this acid was obtained by Divers (Proc. Roy. Soc. 1871, 19, 425) by reduction of the nitrate (*v.* also Maumené, Compt. rend. 1870, 70, 146). The free acid is prepared—

(1) By condensation of nitrous acid with hydroxylamine, usually the sodium or silver salt with the sulphate or hydrochloride, in aqueous solution (Wislicenus, Ber. 1893, 26, 771; Paal, *ibid.* 1026) or free hydroxylamine and N_2O_3 in methyl alcoholic solution (Kauffmann, Annalen, 1898, 299, 98).

(2) By oxidation of hydroxylamine—

(*a*) With metallic oxides, as CuO, HgO, Ag_2O (Hantzsch and Kauffmann, *ibid.* 1892, 292, 317);

(*b*) With sodium hypobromite (Kolotow, J. Russ. Phys. Chem. Soc. 1891, 23, 1, 3).

(3) By reduction of NO, HNO_3, and, still better, HNO_2. A dilute sodium amalgam is used, and the temperature kept low. The hyponitrite is most stable in excess of alkali. After reduction any hydroxylamine formed is destroyed by HgO, and the liquid, after neutralising with HNO_3, precipitated with $AgNO_3$, or the hydroxylamine may be further reduced by sodium amalgam, and the ammonia removed by evaporation *in vacuó* over sulphuric acid.

(4) By alkaline hydrolysis of certain oxyamino- compounds, $OH{\cdot}NH{\cdot}SO_3H$ (Divers and Haga, Chem. Soc. Trans. 1899, 77),

$$OH{\cdot}NH{\cdot}SO_2C_6H_5$$

(Piloty, Ber. 1896, 29, 1559); $OH{\cdot}N{=}NO_2H$ (*q.v.*) behave in this way.

The most convenient procedure is to treat the sodium salt of hydroxylamine disulphonic acid (easily obtained by the action of sulphurous acid on sodium nitrite) with concentrated or fused alkali, when it is obtained by precipitation with $AgNO_3$ as the silver salt in 60 p.c. yield (Kirschner, Zeitsch. anorg. Chem. 1897, 16, 424; *v.* also Hantzsch and Sauer, Annalen, 1898, 299, 89; Wieland, *ibid.* 1903, 329, 225). The methods described for the reduction of nitrites by aluminium amalgam, iron hydroxide, and fusion with iron filings are useless.

The free acid may be isolated by decomposing the silver salt with an ethereal solution of hydrochloric acid, and evaporating the filtrate in a desiccator. It is thus obtained in white, crystalline leaflets, very explosive, decomposing on friction, contact with solid KOH or acid vapours, and often spontaneously.

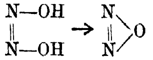
It dissolves very readily in water, readily in alcohol, and is fairly soluble in most organic solvents.

Its decomposition into N_2O and H_2O is not reversible. Small amounts of nitric and nitrous acids are formed at the same time (*v.* further Rây and Ganguli, Chem. Soc. Trans. 1907, 1886; Divers, Chem. Soc. Proc. 1908, 16). Heat of formation $2N+O+Aq.=H_2N_2O_2Aq.$ −57,400 cal. (Berthelot, Ann. Chim. Phys. 1889 [vi.] 18, 571). It can be oxidised to nitric acid by bromine and by $KMnO_4$. It is not reduced by sodium amalgam (Divers), but yields hydrazine with sodium bisulphite (*v.* Brackel, Ber. 1900, 33, 2115).

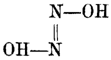
It forms neutral and acid salts, the latter very unstable, only the acid ammonium salt being known in the pure state. The neutral salts are mostly insoluble in water, and can be obtained by precipitation. Esters of hyponitrous acid are obtained by action of the iodide on silver hyponitrite.

The *ethyl ester* is a yellow oil (Zorn, Ber. 1878, 11, 1630), and the *benzyl ester* a low-melting solid (Hantzsch and Kauffmann, *l.c.*).

Constitution.—The molecular weight determined by the cryoscopic method corresponds with the formula $H_2N_2O_2$, which, with its modes of formation and acid properties points to its being *diazodihydroxide.* Hantzsch considers it to be the anti-form, assigning the syn-structure to the isomeric *nitramide* (*q.v.*) owing to the great ease with which even salts of the latter evolve N_2O in solution—



Nitramide.



Hyponitrous acid.

Nitric acid HNO_3. This is, with the exception of ammonia, the earliest compound of nitrogen investigated, its preparation being known to the Egyptians. In the ninth century Geber obtained it by distilling nitre with blue vitriol and alum, and it was known under various names, such as *aqua fortis*, *spiritus nitri acidus*, and *spiritus nitri fumans Glauberi.* Its composition was investigated by Lavoisier (1776) and by Lavoisier and Priestley (1784–1786).

Occurrence.—It is found in nature in combination with NH_4, Na, K, Ca, Mg, and in smaller quantities with Al and Fe. It is produced by atmospheric electrical discharges, and by oxidation of nitrogenous organic matter through the medium of nitrifying bacteria, subsequently combining with ammonia in the air, and with the various bases present in the soil, and occurs in largest quantity as Chile saltpetre ($NaNO_3$) and Bengal saltpetre (KNO_3).

Preparation.—Being the highest oxidation product of nitrogen it is produced by the action of suitable oxidising agents upon all the less oxygenated compounds.

Ammonia is oxidised to nitric acid by atmospheric oxygen in presence of catalytic agents such as $Cu(OH)_2$, Cu, Fe, Ni, Pt (Kuhlmann, Annalen, 1839, 29, 281; Schonbein, J. pr. Chem. 1859, 70, 129; Kraut, Annalen, 1856, 136, 69). Lead manganate and permanganate, sodium manganate and lead chromate also bring about this oxidation (Motay, Ber. 1871, 4, 891; Schwarz, Dingl. poly. J. 1875, 218, 219) upon which principle the patents of Ostwald (Eng. Pat. 698) and Bayer and Co. (D. R. P. 168272) depend.

According to Schmidt and Bocker (Ber. 1906, 39, 1366) the primary oxidation product is NO (*v.* further Smith, Chem. Soc. Trans. 1906, 473).

Ammonia gas is oxidised by heated MnO_2 and Fe_2O_3 to ammonium nitrate, and its solution by ozone, H_2O_2, H_2CrO_4, $KMnO_4$, and by electrolytic and biochemical oxidation.

Nitrous acid is similarly oxidised to nitric acid. Nitrogen and its lower oxides are only oxidised by oxygen to N_2O_4, unless water is present, when nitric acid is formed (*v.* also NITRIC ACID, MANUFACTURE OF; ATMOSPHERIC, NITROGEN, UTILISATION OF).

Properties.—By distillation in a current of CO_2, 98 p.c. acid can be obtained. Fractional crystallisation gives a product with maximum purity of 99·4±0·1 p.c. Absolute nitric acid only exists in the form of snow-white crystals, m.p. −41°. On melting, a yellow liquid results which is a solution of nitric anhydride and water in nitric acid (Kuster and Munch, Zeitsch. anorg. Chem. 1905, 43, 350).

The most concentrated acid may be obtained by distilling the ordinary acid with twice its volume of sulphuric acid in a vacuum apparatus of glass, protected from light.

The physical properties show discontinuities which point to the existence of various hydrates. The freezing-point curve, constructed from the values of Pickering (Chem. Soc. Trans. 1893, 63, 436) and Küster and Kremann (Zeitsch. anorg. Chem. 1905, 41, 1), shows two maxima, at −18·5° and −38°, corresponding to

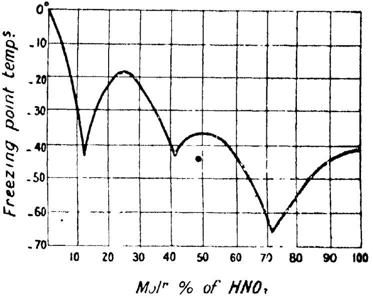
$$HNO_3,3H_2O$$

and HNO_5,H_2O respectively; and three minima, corresponding to the cryohydrates (1) ice $+HNO_3,3H_2O$ (m.p. −43°); (2)

$$HNO_3,3H_2O+HNO_3,H_2O$$

(m.p. −42°); and (3) HNO_3,H_2O+HNO_3 (m.p. −66°).

The existence of these hydrates was, however, signalised as far back as 1783 by Cavendish (Phil. Trans. 76, 1786, 241; 78, 1788, 166). *See* The Scientific Papers of the Hon. Henry Cavendish, Cambridge University Press, 1921.



According to Erdmann (Zeitsch. anorg. Chem. 1902, 32, 431; Zeitsch. angew. Chem. 1903, 16, 1001) orthonitric acid $N(OH)_5$ crystallises in needles, stable below −15°, m.p. −35°, b.p. 40°–40·5°/13 mm. Octobasic nitric acid $O[N(OH)_4]_2$, m.p. −39°, tribasic nitric acid $O{=}N(OH)_3$, m.p. −34°, and tetrabasic nitric acid $O[NO(OH)_2]_2$, m.p. −65·2°, are also described. Independent evidence for the existence of the ortho-acid is obtained from the refractive index curve (Veley and Manley, Proc. Roy Soc. 1901, 69, 86; Chem. Soc. Trans. 1903, 1015), and from the absorption spectra (Hartley, Proc. Roy. Soc. Dublin, 1905, [ii.] 10, 373), but the existence of the polybasic acids is disputed (Kuster and Kremann, Zeitsch. anorg. Chem. 1904, 41, 1; Küster, Zeitsch. angew. Chem. 1903, 16, 1079).

The freezing-points of dilute solutions and the corresponding dissociation values are given by Jones (Zeitsch. physikal. Chem. 1893, 12, 630) and Jones and Getman (Amer. Chem. J. 1902, 27, 433). The change in the value of the molecular lowering with concentration is indicated by the following selected values—

Gram mols. HNO_3 per litre	Molecular lowering
0·001054	3·7951°
0·01153	3·7294°
0·1059	3·5269°
0·25	3·501°
0·5	3·621°
1·0	3·796°
2·0	4·174°
3·0	4·603°

The densities, and the changes in density with temperature, of nitric acid solutions of different concentrations have been determined by Lunge and Rey (Zeitsch. angew. Chem. 1891, 165) and Veley and Manley (*l.c.*), and afford further evidence of the existence of hydrates (Veley and Manley). *Cf.* Bousfield, Chem. Soc. Trans. 1915, 1405.

The following table is constructed from Lunge and Rey's values—

$d_4^{15°}$	p.c. HNO_3	$d_4^{15°}$	p.c. HNO_3
1·00	0·10	1·30	47·49
1·05	8·99	1·35	55·79
1·10	17·11	1·40	65·30
1·15	24·84	1·45	77·28
1·20	32·36	1·50	94·09
1·25	39·92	1·52	99·67

Density of normal HNO_3 solution (63·13 grams per litre)=1·0318 at 18·6° (Kohlrausch, Wied. Ann. 1865, 26, 161), 1·0324 at 18° (Loomis, *ibid.* 1897, 60, 532).

The expansion of dilute solutions with temperature has been studied by Forch (Wied. Ann. 1895, 55, 100) and Ostwald (J. pr. Chem. 1877, [ii.] 16, 385), and that of concentrated solutions by Kuster and Kremann, who find two breaks in the otherwise continuous concentration, at 54·0 p.c. HNO_3 and 77·77 p.c. HNO_3, corresponding to $HNO_3,3H_2O$, and HNO_3,H_2O respectively.

The density of nitric acid increases with the addition of nitrogen peroxide (Lunge and Marchlewsky, Zeitsch. angew. Chem. 1912, 10), reaching a maximum when the mixture contains about 12·5 p.c. by weight of the peroxide. This corresponds with a hydrate, $N_2O_5{\cdot}N_2O_4,H_2O$, the existence of which is confirmed by a thermal study of the reciprocal solubilities of nitric acid and nitrogen peroxide. This hydrate is stable below −48·5°, but at this temperature dissociates, liberating nitrogen peroxide (Pascal and Garnier, Bull. Soc. chim. 1919, [iv.] 25, 309).

For the conductivity of nitric acid solutions, *v.* Kohlrausch (Wied. Ann. 1885, 26, 161), Arrhenius (Zeitsch. physikal. Chem. 1889, 4, 96), Loomis (Wied. Ann. 1897, 60, 547), Veley and Manley (Proc. Roy. Soc. 1897, 62, 223), and Küster and Kremann (*l.c.*). The existence of the above hydrates is again indicated; two irregularities in the conductivity curve occurring at 25 and 50 mols. p.c. HNO_3, corresponding to the compounds $HNO_3,3H_2O$ and HNO_3,H_2O respectively, and a third at 96–100 p.c. HNO_3, at which concentration irregularities also occur in the density and freezing-point curves, pointing to the commencement of anhydride formation previously mentioned.

Nitrates dissolved in concentrated nitric acid increase its conductivity in proportion to the amount dissolved (Bouty, Compt. rend. 1888, 106, 595, and 654).

The viscosity of nitric acid has been determined by Graham (Phil. Trans. 1861, 153, 373), Reyher (Zeitsch. physikal. Chem. 1888, 2, 744), Paggliani and Oddone (Wied. Ann. Beibl. 11, 415), and Kuster and Kreman (*l.c.*). The last-named give the following values $\eta=1$ for water at 0°—

p.c. HNO_3	98·5	82·0	70·0	65·0	50·0	30·0	10·0	0 0
η (+15°)	0·548	1·036	1·277	1·300	1·144	0 822	0·655	0·667
η (−15°)	0·833	2·241	3·268	3·304	2·369	1·635	—	—

Cf. Bousfield (Chem. Soc. Trans. 1915, 1781), who gives the viscosities of a series of nitric acid solutions at various temperatures.

The maximum at about 65 p.c corresponds to the constant boiling mixture $2HNO_3,3H_2O$ first investigated by Dalton. It is not a compound, its composition varying with the pressure. At 735 mm. it contains 68·0 p.c. HNO_3 (b.p. 120·5°) and at 1220 mm. 68·6 p c. HNO_3 (Roscoe, Annalen, 1860, 116, 203), while, by passing indifferent gases through the acid at ordinary temperatures residues differing still more widely in composition are obtained.

The vapour tensions of nitric acid solution have been determined by Saposhnikoff (Zeitsch. physikal. Chem. 1905, 53, 225). For the higher concentrations they are as follows :—

d_4	p c. HNO_3	p c. H_2O	p (mm. at 15°)	p.c. N in vapour
1·400	65·30	34·70	1·90	19·32
1·453	78·10	21·90	9·40	22·52
1·462	82·10	17·90	16·64	22·65
1·487	88·65	11·35	29·70	23·05
1·497	92·93	7·07	42·60	23·50
1·510	98·00	2·00	46·20	23·75

As HNO_3 contains only 22·22 p.c. N, oxides are also present in the vapour.

Determinations of the boiling-point of aqueous solutions of nitric acid at different pressures have been made by Creighton and Githens, J. Franklin (Inst. 1915, 179, 161), Creighton and Smith (*ibid.* 1915, 180, 703).

With mixtures of nitric and sulphuric acids the vapour tension rises and then falls with increasing percentages of HNO_3. The maximum for HNO_3 of sp.gr. 1·40 occurs at 45 p.c. HNO_3 (23·5 mm.), and for HNO_3 of sp.gr. 1·48 at 67 p.c. HNO_3 (34 mm.). With the pure acids the value rises steadily to 41 mm. at 80 p.c. HNO_3, remains constant up to 92 p.c., and rises subsequently to 46 mm. with pure HNO_3 (Saposhnikoff, *ibid.* 1904, 49, 697; 1905, 51, 609; *cf.* Pascal, Compt. rend. 1917, 165, 589). The purest obtainable nitric acid boils at 86° with partial decomposition. Under 24 mm. it boils at 21·5° (Erdmann, Zeitsch. anorg. Chem. 1902, 32, 431).

Refractive index.

$d_4^{20°}$	D line	Mol. dispn.
1·50999	1·39584	0·338
1·50875	1·36870	0·340

(Brühl, Zeitsch. physikal. Chem. 1897, 22, 373) The maximum value (1·4061 at 14·2°) is shown by 70 p.c. HNO_3, while the values for 50 p.c. and 99 p.c. acid are practically identical (Veley and Manley, Proc. Roy. Soc. 1901, 69, 86).

For the absorption spectra, *v.* Hartley, Chem. Soc. Trans. 1903, 658.

Heat of formation.—

$$\mathrm{H+N+O_3+Aq.=HNO_3Aq.}+49{,}090 \text{ cal.}$$

(Thomsen), 48,800 (Berthelot), which, by subtracting the heat of solution (7490, Thomsen; 7180, Berthelot) gives

$$\mathrm{H+N+O_3=HNO_3}+41{,}600 \text{ cal.}$$

Mol. heat of evaporation 7250 cal., mol. heat of fusion 600 cal. (Berthelot, Ann. Chim. 1877, [v.] 12, 530).

Nitric acid is decomposed by light into oxygen, nitrogen peroxide, and water (Berthelot, Compt. rend. 1898, 127, 143; Veley and Manley, Phil. Trans. 1898, 191, 365; Reynolds and Taylor, Chem. Soc. Trans. 1912, 101, 131). The vapour is more prone to decomposition than the liquid and the reaction is reversible, the products of the decomposition by light recombining in the dark. Anhydrous nitric acid (100 p.c) decomposes spontaneously in the dark:

$$\mathrm{4HNO_3 \rightleftarrows 2N_2O+2N_2O_4+O_2}$$

Specific heat.—

p c HNO_3	58 3	12 3	3 4	26	15	3 4
Sp.ht. .	0·6651	0·8752	0·9618	0·768	0·849	0·963

The first three are Marignac's values at 21°–52° (Annalen, 1872 (suppl.), 8, 335), the last three Thomsen's at 18°.

Chemical properties.—Nitric acid has been shown by the usual methods (rate of hydrolysis of methyl acetate, inversion of cane sugar, freezing-point lowering and conductivity) to be the strongest known acid. Accordingly it has a high value for its heat of neutralisation (with NaOH 13,680 cal.; with KOH 13,770 cal. Thomsen, Th.U 1906, 40). Its heat of dissociation for $v=1·5–6$ is about 2800 cal. (Petersen, Zeitsch. physikal. Chem. 1893, 11, 174), for $v=10$ about 1362 cal. (Arrhenius, *l.c.*).

It dissolves readily in ether, and the ether-water partition coefficients have been determined by Bogdan (Zeitsch. Elektrochem. 1905, 11, 824; 1906, 12, 489; *v.* also Hantzsch and Sebaldt, Zeitsch. physikal. Chem. 1899, 30, 285). The molecular weight in ethereal solution is normal.

The nitrate ion is one of the most electronegative ions. Migration velocity 61·8 at 18° (Landolt-Börnstein, 1905, 237). All its salts are soluble, and there is little tendency to form complexes.

The chief characteristic of nitric acid is its remarkable oxidising power, being itself capable of reduction to HNO_2, NO_2, NO, N_2O, $H_2N_2O_2$, NH_2OH, N_2, and NH_3. Ostwald (Grundliss. d. allgem. Chemie, 1899, 440) explains the formation of these products on the supposition that nitric acid can so dissociate that it forms OH ions with the loss of positive charges—

$$\begin{array}{lll}
\mathrm{HNO_3} & \rightarrow \mathrm{NO_2+OH'} & \rightarrow \mathrm{NO_2+OH'}+\oplus \\
 & \nearrow \mathrm{NO_2H''+2OH'} & \rightarrow \mathrm{NO_2H+2OH'}+2\oplus \\
\mathrm{NO(OH)_3} & & \\
 & \searrow \mathrm{NO'''+3OH'} & \rightarrow \mathrm{NO+3OH'}+3\oplus \\
 & \nearrow \mathrm{NOH''''+4OH'} & \rightarrow \dfrac{\mathrm{(NOH)_2}}{2}+\mathrm{4OH'}+4\oplus \\
\mathrm{NO(OH)_5} & & \\
 & \searrow \mathrm{N'''''+5OH'} & \rightarrow \dfrac{\mathrm{N_2}}{2}+\mathrm{5OH'}+5\oplus
\end{array}$$

The oxidation potential (Ihle, Zeitsch. physikal. Chem. 1896, 19, 589) is lowered by the presence of nitrous acid, which, however, increases the rate of oxidation.

Nitric acid is not affected by hydrogen at ordinary temperatures or at 100° (Berthelot, Compt. rend. 1898, 127, 27), but is reduced by it to ammonia in presence of platinum sponge (Wagner, Dingl. poly. J. 1867, 183, 76). The concentrated acid oxidises boron on slightly warming to boric acid with evolution of NO and N_2, carbon to carbon dioxide, in the cold if finely divided, phosphorus to phosphorous, and finally to phosphoric acid (when, according to Montemartini, Gazz. chim. ital. 1898, 28, i. 397, ammonia is also produced). Sulphur is oxidised to H_2SO_4 with great readiness if finely divided, selenium to H_2SeO_3, and iodine to iodic acid with production of nitrous acid. Hydrides are also oxidised: PH_3 readily, H_2S only if NO_2 be present (acid of sp.gr. 1·18 free from NO_2 has no action: Kempf, Annalen, 1857, 102, 342), SeH_2 violently (Hofmann, Ber. 1870, 3, 660). HBr at 0° forms Br_2 and NO_2, HI yields I_2 and NO (HNO_2 in dilute solution, Eckstädt, Zeitsch. anorg. Chem. 1901, 29, 51) and HCl,NOCl (*q.v.*).

SO_2 reduces HNO_3 readily, some N_2O being formed. In presence of dilute sulphuric acid reduction is still more readily effected, with evolution of NO, and in presence of concentrated H_2SO_4 nitrosyl sulphuric acid (Weber, Pogg. Ann. 1867, 130, 277).

Ferrous salts yield NO, stannous salts NH_2OH, and NH_3, $AsCl_3$ and As_4O_6 arsenic acid, and $SbCl_3$ antimonic acid.

Nitric acid attacks with more or less readiness according to their nature, and the concentration of the acid, all metals with the exception of Au, Rh, Ir, and Pt (the last-named when alloyed with other metals goes into solution, *e.g.* an alloy of 4·64 p.c. Pt and 95·35 Hg is entirely soluble, Tarugi, Gazz. chim. ital. 1903, 33, [ii.] 171), much more quickly when the metals remain at rest, when they are rapidly rotated, or the acid is stirred (owing to the fact that in the former case, nitrous acid accumulates in the neighbourhood of the metal) with formation of the nitrate except in the case of Sn, W, Mo, and As, when the anhydride of the corresponding acid is produced, the nitric acid itself being reduced to various stages. Sn forms stannic nitrate first, which breaks up yielding the dioxide. Sb is converted into Sb_2O_4. Briefly it may be stated that with the less reactive metals, such as Hg, Ag, Cu, Bi, reduction to the first stage only takes place, and is probably not due to the agency of nascent hydrogen, but to nitrous acid, the influence of which on the reactivity of nitric acid was first noticed by Millon (J. Pharm. Chim. 1842, [iii.] 2, 179). Thus, with copper—

$$\begin{array}{ll}
\text{(i.)} & \mathrm{Cu+4HNO_2=Cu(NO_2)_2+2H_2O+2NO} \\
\text{(ii.)} & \mathrm{Cu(NO_2)_2+2HNO_3=Cu(NO_3)_2+2HNO_2} \\
\text{(iii.)} & \mathrm{HNO_3+2NO+H_2O=3HNO_2}
\end{array}$$

The nitrous acid thus continuously produced at once decomposes—

$$\mathrm{3HNO_2=HNO_3+2NO+H_2O}$$

nitric oxide being evolved (Veley, Roy. Soc. Trans. 1891, 182, A, 279).

From the equilibrium

$$\mathrm{3NO_2+H_2O \rightleftarrows 2HNO_3+NO}$$

it is evident that with concentrated acid the product is NO_2.

The most complete reduction (to N_2 and NH_3) takes place with the more electro-positive metals such as Sn, Co, Ni, Fe, Cd, Zn. Mn, Mg. Thus Zn and very dilute acid give ammonia, whilst with Sn reduction is less complete, hydroxylamine being one of the products. With more reactive metals, such as Mg, some hydrogen (which may be regarded as the primary product) escapes oxidation. The action is greatly affected by conditions, being slow at first, accelerating as the reduction products, which act catalytically, accumulate. Further, different concentrations yield different products, and hence as the concentration changes during the reaction, mixed products in varying proportions are usually obtained. With Zn, in intermediate concentrations, even nitrous oxide and nitrogen may be found in considerable quantities amongst the gaseous products. For further details, *v.* Acworth and Armstrong (Chem. Soc. Trans. 1877, 32, 54), Montemartini (Atti R. Accad. Lincei, 1892, [v.] 1, i. 63), Walker (Chem. Soc. Trans. 1893, 63, 845), Higley (Amer. Chem. J. 1899, 21, 377), Stillmann (*ibid.* 1897, 19, 711), Bijlert (Zeitsch. physikal. Chem. 1899, 31, 131), Gladstone (Phil. Mag. 1900, [v.] 50, 231), Stansbie (J. Soc. Chem. Ind. 1908, 27, 365; 1909, 28, 274), Rennie (Chem. Soc. Trans 1908, 1162), Dunstan and Hill, passivity in (Chem. Soc. Trans. 1911, 1853).

With alloys of copper and zinc, as long as they contain more than 48 p.c. of copper, the alloy dissolves as a whole. Below this percentage of copper, the zinc either dissolves faster in proportion than the copper or precipitates that metal from solution, with the result that more copper dissolves when the solutions are shaken than when at rest (Stansbie, J. Soc. Chem. Ind. 1913, 32, 1135).

Electrolytic reduction, as shown by Schönbein and Brewster, yields first nitrous acid, and finally ammonia. The nature of the product depends on the temperature, current strength, material of cathode, and its potential, and upon whether the solution is acid or alkaline. With a mercury cathode only hyponitrite is formed (Zorn, Ber. 1879, 12, 1509), with a copper cathode, ammonia (Ulsch, Zeitsch. Elektrochem. 1897, 3, 546).

Nitric acid of 40 p.c. strength containing 1 p.c. of dissolved nitrous gases yields NO (99-100 p.c.) at the cathode on electrolysis (Meister, Lucius and Brüning. Eng. Pat. 10522, May 1, 1911; *v.* Müller and Weber, Zeitsch. Elektrochem. 1903, 9, 955; Müller, *ibid.* 978; Müller and Spitzer, *ibid.* 1905, 11, 509; Ber. 1905, 38, 1190; and Tafel, Zeitsch. anorg. Chem. 1902, 31, 289). The mechanism of the reaction is not clearly understood. Tafel finds that though nitric acid is reduced only to NH_2OH by mercury or well-amalgamated electrodes, copper reduces it to ammonia, and yet has no action on hydroxylamine itself.

Metallic nitrates are normal salts (in only a very few instances are acid or basic salts obtained, and then only under special conditions) which are readily soluble in water, and in many cases in alcohol, or acetone, stable in aqueous solution, and which usually crystallise in the anhydrous form.

Nitric acid forms nitro derivatives with many organic compounds, and with alcohols yields esters.

On contact with the skin substances of bright yellow colour (xantho-proteic acids) are produced. Its chemical properties are best represented by the formula $H{-}O{-}N{<}^{O}_{O}$.

Commercial nitric acid, made from Chile nitrate, occasionally contains minute quantities of tetranitromethane, monochlorotrinitromethane, and dichloroditromethane, probably due to traces of chlorides and organic matter in the sodium nitrate employed (Crawford, J. Soc. Chem. Ind. 1922, 321, T.).

Estimation (*v.* ANALYSIS).—The most characteristic test is the red colour developed with brucine and concentrated H_2SO_4. Arbutin and berberine under similar conditions yield a deep yellow and a dark brownish-red colour respectively (Reichard, Chem. Zeit. 1906, 30, 790).

Cinchonamine nitrate is nearly insoluble in water (Howard and Chick, J. Soc. Chem. Ind. 1909, 28, 53).

Di-9-10-monoxyphenanthrylamine dissolved in conc. sulphuric acid forms a delicate test for nitric acid in presence of other oxidising substances. As a reagent, 0·1 gram is dissolved in 1 litre of conc. sulphuric acid and 0·1 gr. of the substance to be tested is added to 2 c.c. of the reagent, when, if nitrates be present, the blue colour turns to a claret-red Nitrous acid does not alter the colour unless it becomes oxidised to nitric acid (Schmidt and Lumpp, Ber. 1910, 43, 787 and 791).

Fuming nitric acid. A red, fuming liquid with powerful oxidising properties, produced by adding to concentrated HNO_3, nitrous acid, nitrogen trioxide, or nitric oxide, by distilling nitre with potassium acid sulphate, and also by adding kieselguhr saturated with formaldehyde to the concentrated acid (Vanino, Ber. 1899, 32, 1392).

As prepared by any of these methods it contains free NO_2 (Marchlewski, Zeitsch. anorg. Chem. 1892, 1, 363), and in the case where NO is used may be supposed to be formed either by direct union with oxygen, or as represented by the equation $2NO+HNO_3+H_2O \rightarrow 3HNO_2$, the latter then giving NO_2 with the excess of HNO_3. The intermediate production of nitrous acid is shown by addition of water, when it becomes green, blue, and finally colourless (*v.* further Marchlewski and Liljenstein, Zeitsch. anorg. Chem. 1892, 2, 18; 1894, 5, 288).

The specific gravities of the fuming acid of different NO_2 content are given by Lunge and Marchlewski (Zeitsch. angew. Chem. 1892, 1).

Fuming nitric acid oxidises organic compounds to carbon dioxide and water, any sulphur present being converted into H_2SO_4, and phosphorus into H_3PO_4 (Carius, Ber. 1870, 3, 697).

Aqua regia. First obtained by Geber in the eighth century by dissolving salammoniac in *aqua fortis*. Also formed by mixing HCl and HNO_3. The reaction is represented by

$$HNO_3+3HCl=2H_2O+NOCl+Cl_2$$

(*v.* Tilden, J. 1874, 214); Goldschmidt, Annalen, 1880, 205, 372). So named on account of its solvent action on the noble metals.

Pernitric acid HNO_4 is said to be obtained as the silver salt as a black crystalline mass on electrolysing $AgNO_3$ solution (Mulder and Heringa, Rec. trav. chim. 1898, 17, 129). Its existence is doubtful.

ACID HALIDES OF NITRIC ACID.

Nitryl fluoride NO_2F is formed by the action of excess of fluorine on nitric acid at the temperature of liquid air. It is a gas which attacks the mucous membrane, m.p. −139°, b.p. −63·5°; V.d. 2·17-2·31 (air=1) calculated for NO_2F 2·26 It does not combine with hydrogen, sulphur, or carbon, but attacks boron, silicon, phosphorus, arsenic, antimony, iodine, alkali, and alkaline earth metals, aluminium, iron, and mercury. With water the quantitative reaction $NO_2F+H_2O=HF+HNO_3$ takes place It reacts with many organic compounds (Moissan and Lebeau, Compt. rend. 1905, 140, 1573).

Nitryl chloride NO_2Cl (Muller, Annalen, 1862, 122, 1; Odet and Vignon, Compt. rend. 1870, 70, 96) and *nitryl bromide* NO_2Br (Hasenbach, J. pr. Chem. 1871, [ii.] 4, 1) are, according to Gutbier and Lohmann (J. pr. Chem. 1905, [ii.] 71, 182), non-existent.

MANUFACTURE OF NITRIC ACID.

At the present time the nitric acid of commerce is made by one of three processes: viz. (1) decomposition of sodium nitrate, (2) burning of ammonia in oxygen in the presence of a catalyst, and (3) union of nitrogen and oxygen in the electric arc. For the third, *see* NITROGEN, UTILISATION OF ATMOSPHERIC.

In the first process, which is still the most important, approximately equal weights of Chile nitre and 66°Bé. sulphuric acid are heated in cast-iron retorts and the resulting vapours condensed. The residue consists of a fused mixture of sodium sulphate and sodium hydrogen sulphate, and if over-heated, may also contain sodium disulphate ($Na_2S_2O_7$). This residue is discharged into iron pans, where it solidifies; or it may be run into the pan of a hydrochloric acid furnace, where it is converted into salt-cake by reacting with salt. A part of the nitre-cake now produced is converted into sodium sulphide and into a mixed sodium sulphate-ammonium sulphate fertiliser.

Since the heat of vaporisation of nitric acid is low, the nitric acid vapour is easily condensed. The vapours from the retort contain also nitrogen peroxide from the decomposition of nitric acid by heat (Carius, Annalen, 1873, 169, 273), according to the equation:

$$4HNO_3+heat=2H_2O+4NO_2+O_2$$

They also contain air which leaks into the system owing to the reduced pressure maintained therein. The nitrogen peroxide tends to dissolve in the acid condensed in the condenser and to form nitrous acid. The water formed in the above reaction, as well as that originally in the raw materials, condenses with the nitric acid. The remaining gases pass the condenser, tending to carry with them uncondensed nitric acid vapour

Notwithstanding the presence of water in the charge, the first distillate is strong, becoming weaker as the distillation proceeds, until at the end it is almost pure water. The greatest evolution of nitrogen peroxide also occurs in the beginning, and as this is most soluble in strong nitric acid, it would contaminate the final product unless some means were taken to remove it. This is usually accomplished by so condensing that the condensate is removed from the system hot. Thus the nitrogen peroxide remains in the system, passes through the condenser with the uncondensed gases, and must be absorbed in an absorption system.

Retorts.—Nearly all modern retorts are vertical pots suspended in a brick setting They are made of cast iron which is not attacked by nitric acid vapour, or appreciably corroded by the sulphuric acid in the charge Fig. 1 shows one type of retort and setting, arranged for coal firing. Gas firing is also extensively used, presenting the advantages of greater fuel economy and readier control, but is not justified except for large plants.

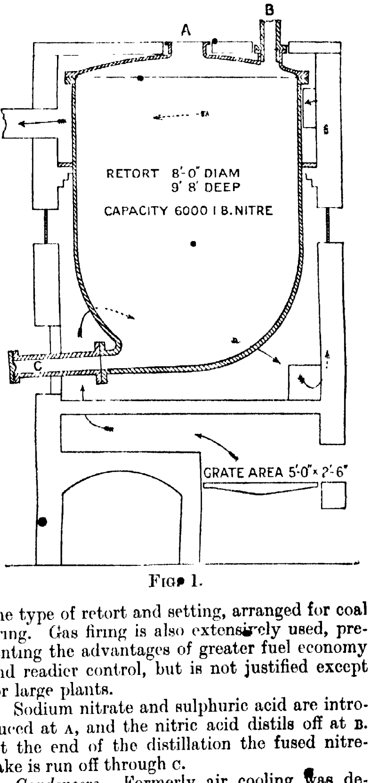


FIG. 1.

Sodium nitrate and sulphuric acid are introduced at A, and the nitric acid distils off at B. At the end of the distillation the fused nitre-cake is run off through C.

Condensers.—Formerly air cooling was depended upon altogether, but modern practice makes use entirely of water cooling. Many forms of water-cooled condensers have been proposed, but only two are in common use. These are the glass condenser of Hart (U.S. Pat. 525761, 1894) and S-bend condensers made of silica or silicon-iron alloys.

A Hart condenser is shown in Fig. 2. It consists of two upright manifolds of chemical-ware or silicon-iron, connected by parallel glass tubes 3 inches diam. by 6 feet long. These are packed into the manifolds with a plastic putty made of oil-ground white-lead, 10 lbs.; red-lead, 1 lb.;

linseed oil, 3 gals.; and asbestos fibre enough to give proper consistency. Water is allowed to trickle over the outside of the tubes, being delivered through the pipe A, and is kept from splashing by wooden guides hung between the tubes and shown in detail at B and in cross section at C. The hot water from the condenser is caught in the trough D and escapes to the drain through E.

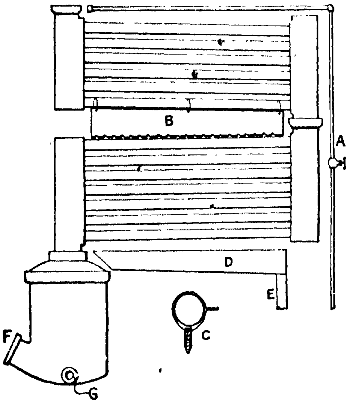


Fig. 2.

The tube breakage amounts to about 100 per retort per year. It is heaviest with weak charging acid. Broken tubes may be replaced while running.

In principle the S-bend condenser is the same as the Hart condenser, its construction being shown in Fig. 3, a Y-tube branching from the top of the bleacher to two parallel series of S-bends, 6 inches in diam. and 6 feet long. This type possesses the advantage over the Hart condenser of having fewer joints and of these being all horizontal. Even with no putty packing in the joints there is no tendency to lose acid by leakage.

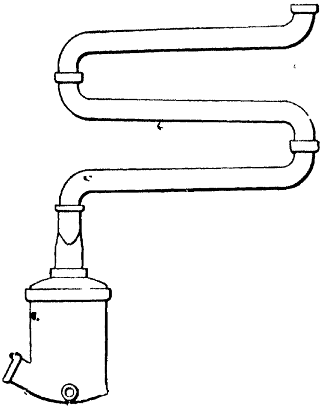


Fig. 3.

While the silica S-bends are lighter and cheaper than those of silicon-iron, they are much more fragile, and hence must be handled with extreme care. The latest practice favours the S-bend condenser of silicon-iron above all others.

Bleaching.—Most of the uses to which nitric acid is put require that it be as free as possible from nitrous acid. To remove this it was formerly the practice to warm the acid while blowing a current of air through it. This, however, required a separate operation, which is now avoided (Skoglund, U.S. Pat. 591087, 1897) by allowing the condensed acid to reflux through a bleacher while still hot. Here it encounters the hot gases from the retort, which further heat it, driving out the dissolved nitrogen peroxide. The acid running from the bleacher contains, on an average, about 1 p.c. nitrous acid.

Fig. 2 shows the relation of the bleacher to the condenser. The gases from the retort enter at F, rise through the packing in the bleacher and are condensed in the condenser. The condensate drains back through the bleacher counter-current to the gases and emerges at G.

Absorption.—Even with the most careful attention to details, from 6–10 p.c. of the nitrogen content of the nitrate passes the condenser in the form of nitrogen peroxide. In the absorption system this is converted to nitric acid.

The absorption system consists of a series of chemical-ware towers filled with an acid-proof packing material, where the gas is subjected to a systematic scrubbing with dilute nitric acid. This system is so arranged that the strongest gas comes in contact with the strongest acid, and the weakest gas with almost pure water. In these towers the following reactions occur:

$$(1)\ 3NO_2+H_2O \rightleftarrows 2HNO_3+NO$$
$$(2)\ 2NO+O_2=2NO_2$$

The first is an equilibrium which is established practically instantly (Burdick and Freed, J. Amer. Chem. Soc. 1921, 43, 518–30), while the second goes to completion, but requires considerable time to do so (Burdick, J. Amer. Chem Soc. 1922, 44, 244–51). Given sufficient time, the nitrogen peroxide can thus be quantitatively converted into nitric acid, but, practically, owing to the slowness of the second reaction and the necessarily limited reaction space in the towers, this is never accomplished, 95 p.c. conversion being considered good practice.

The absorption tower construction is shown in Fig. 4. The tower consists of 6 sections of chemical-ware about 30 inches in diameter and 30 inches high. The bottom section rests in a saucer mounted on a pedestal. The gas enters the tower at A, rises through the packing rings generally used to fill the tower and leaves the tower through the pipe B. Acid is continually circulated over the tower by the air-lifts C, supplied with acid from the equaliser pot D. The acid draining from the tower enters this pot from behind; any excess above that in circulation, which may enter from the next equaliser pot D′, or be formed in the tower, is removed continually by the air-lift E.

An absorption system consists of a series of such towers, each set higher than its predecessor, so that the weak acid may drain toward the acid exit of the system. The ratio of towers to 6000 lbs. retorts is usually 1·2 : 1–1·5 : 1.

Draught is maintained on the system by an air-jet exhauster in the exit from the last tower, by a steam jet, or, best, by an acid-proof fan driven by an electric motor.

Operating data.—The best strength of charging acid to use with dry nitre is 92·5 p.c. (Winteler, Chem. Zeit. 1905, 29, 820–23). With wet nitre the strength of the acid should be increased proportionally to the water content. Either stronger or weaker acid results in a dilute distillate

With a ratio of $H_2SO_4 : NaNO_3 = 1$ and acid of the above strength the British nitric acid plants during the war produced a distillate of 90–92 p.c. HNO_3, constituting about 90 p.c. of the acid made. The remaining 10 p.c. was weaker, containing 60–80 p.c. HNO_3. The overall yield was from 94–96 p.c., the nitre cake acidity varied from 27–31 p.c. H_2SO_4, and the coal consumption was about 0·185 lb. per lb. 100 p.c. HNO_3 with gas firing and about 0·325 with direct firing. Using a nitre charge of 5000–5300 lbs. the time of a complete cycle was 18–24 hours (Ministry of Munitions, Department of Explosives Supply. Report on the Statistical Work of the Factories Branch, H.M. Stationery Office, London).

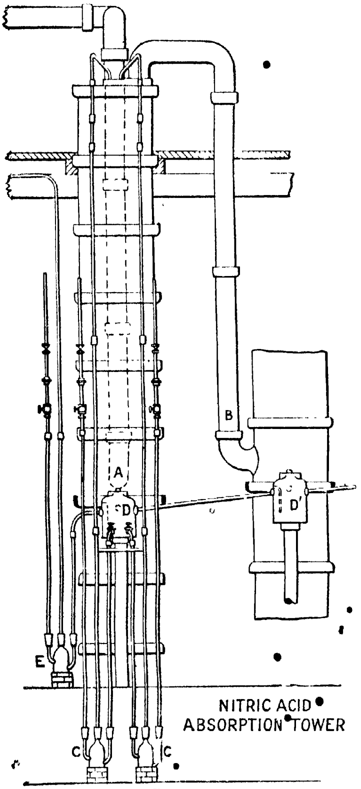


FIG. 4.

In the United States (Zeisberg, Chem. Met. Eng. 1921, 24, 443–45) the cycle of operations with a 7000-lb. nitre charge requires only 12 hours. The yield is also somewhat better, having been 97·6 p.c. there during war-time pressure, and is now approximately 99 p.c. The coal consumption with direct firing is about 0·222 lb. per lb. 100 p.c. HNO_3 with continuous operation, and 0·265 with one-shift operation. The labour requirements are low, being 1·9 men-hr. per 1000 lbs. HNO_3 with single shift, and 1·4 men-hr. with continuous operation. Without separation of the strong distillate and the weak absorption tower acid, the average strength of the whole output is 88–90 p.c. HNO_3, with about 1 p.c. NO_2.

Full design data, with many detailed drawings, for British nitric acid practice, may be found in Preliminary Studies for H.M. Factory, Gretna, published by H.M. Stationery Office, London.

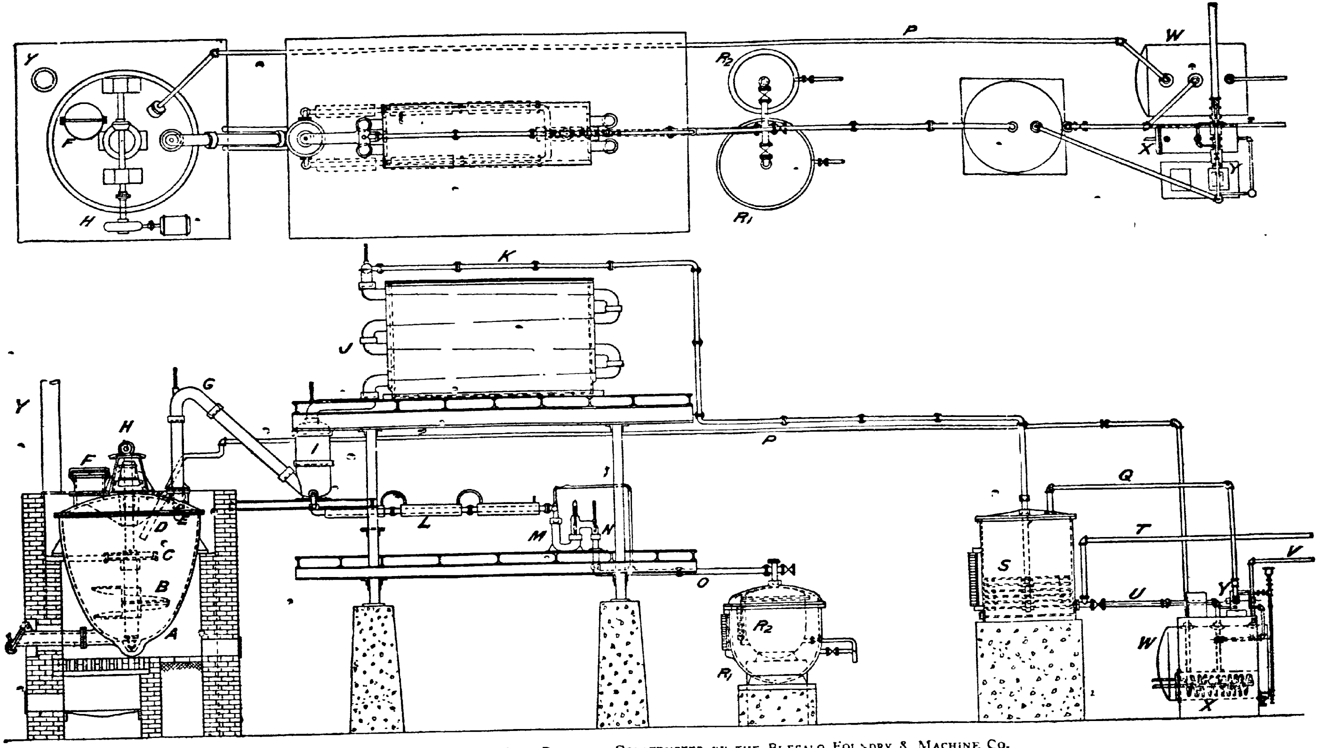
Vacuum processes.—In order to carry out the decomposition of the nitre at a lower temperature, and thus avoid thermal decomposition of the nitric acid, Valentiner (D. R. P. 63207, 1891; Eng. Pat. 4254, 1907; U.S. Pat. 920224, 1909) proposed carrying out the decomposition in a vacuum. His process was fully described in the last edition of the DICTIONARY.

During the war this process was considerably developed in Germany by Frischer, principally in the direction of increasing the size of the apparatus and substituting a rotary liquid sealed pump for the older reciprocating pump, which was always a source of annoyance.

A further improvement on the vacuum process has been made by Hough (Worden, Technology of Cellulose Esters, Vol. I. Part 2, pp. 826–34, 1921), by introducing a stirring device into the retort. His whole apparatus is shown in Fig. 5.

A nitre charge of 5000 lbs. is placed in the retort, and the stirrer, B, and vacuum pump, Y, are started. Sulphuric acid, which has first been used in the scrubber, S, and the pump-tank, X, is then added from tank, W, 5400 lbs. of 92·5 p.c. acid being used The gases pass from the retort through E to the bleacher, I, and thence to the condenser, J. The uncondensed gases pass to the scrubber, S, where they are scrubbed with sulphuric acid; then through the pump, Y, of the rotary, sulphuric acid sealed type, to the atmosphere. The scrubbing acid in S is next used to seal the pump, and is then used for charging acid. The hot acid from the bleacher runs through the coolers, L, to the receivers, R_1 and R_2. When the distillation is completed, as shown by the hydrometer in the still-watcher, M, the vacuum (usually about 20 inches Hg) is broken, the temperature of the charge is raised to melt the nitre-cake, and it is run out.

It is claimed that five charges can be handled per 24 hrs. The whole of the distillate is obtained at a strength of about 91 p.c., and practically free from nitrous acid. The yield is about 97 p.c. (since no absorption system is used) and the fuel consumption about 0·075 lb. per lb. 100 p.c. nitric acid, which is remarkably low. The stirrer consumes from 1½–2 kw., and the pump about 4 kw.



The Hough Nitric Acid Plant, as Constructed by the Buffalo Foundry & Machine Co.
Fig. 5.

Other processes.—Considerable work has been done (Guye, Eng. Pats. 131335, 131336, 1919; Norsk Hydro, D. R. P. 340360, 1921) on making nitric acid from nitrogen peroxide obtained from the arc process of nitrogen fixation, or from ammonia oxidation, according to which the peroxide is liquefied and treated under pressure in an autoclave with water and oxygen. Highly concentrated nitric acid is thereby obtained, which is not the case when nitrogen peroxide is recovered in an ordinary absorption system.

Ammonia oxidation.—During the war there **was a great development of the so-called Ostwald process of oxidising ammonia. An air stream, containing 10 p.c. of ammonia, is passed through a platinum gauze maintained at a red heat by the heat of the reaction, or, according to Landis (U.S. Pat. 1193797, 1915), by the passage of an electric current through the gauze.** The ammonia reacts with the oxygen of the air according to the equation:

$$(3)\ 4NH_3+5O_2=6H_2O+4NO$$

The resulting nitric oxide is converted to nitric acid by oxidation to nitrogen peroxide according to equation (2), and absorption in water according to equation (1), yielding a 50 p.c. nitric acid.

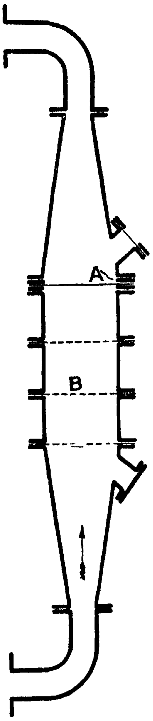


Fig. 6

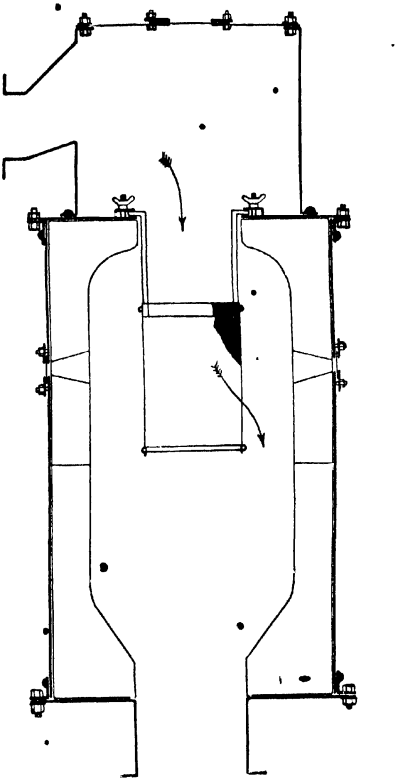


Fig. 7.

With a pure ammonia gas the conversion proceeds smoothly, but there are a number of contact poisons, of which the worst is phosphine. Iron oxide, grease, tar, &c., should be kept off the gauze. With pure gas and good operating conditions about 90 p.c. of the ammonia is converted to a recoverable form, the remainder being reduced to elemental nitrogen and lost. Once having obtained nitric oxide the gas is cooled quickly, to remove the water; it is allowed to oxidise, and is then absorbed in water in the usual way.

In Great Britain a number of ammonia oxidation installations have been made in connection with the nitrogen oxide supply to lead-chamber sulphuric acid plants, for which purpose this process is ideally adapted. For most uses the nitric acid yielded by this process is too weak and must be concentrated, an expensive process at best. Nevertheless, Germany obtained a large proportion of her nitric acid by ammonia oxidation during the war, using, for lack of platinum, a catalyst made up of ferric oxide activated by the addition of manganese and bismuth oxides.

Fig. 6 shows an oxidiser of the flat gauze type developed in Great Britain by the Munitions Inventions Department (The Oxidation of Ammonia Applied to Vitriol Chamber Plants, M.I.D. Research Laboratory, 1919), and now in use at various lead-chamber plants. It consists of a separable cast aluminium casing into which is clamped a gauze frame, A. This frame carries a two-layer, 80-mesh gauze of 0·065 mm. pure platinum wire if electrical heating is to be used, and a 4-layer gauze if self-heating is used. The area of the gauze is 4 inches by 6 inches, and about 480 lbs. nitric acid are produced per 24 hrs. The conversion efficiency is 85 p.c. without electrical heating, and 90–95 p.c. with electrical heating. The gas mixture passes in at the bottom and through the aluminium baffles, B, before reaching the gauze.

Fig. 7 shows an oxidiser of the cylindrical gauze type developed in the United States by Jones and Parsons (U.S. Pat. 1321376, 1919; Parsons, J. Ind. Eng. Chem. 1919, 11, 541–52). It consists of an outer cylindrical shell of iron lined with chemical-ware. Into the centre of the space thus formed a cylindrical, 80-mesh gauze of 4 layers, made of 0·0026-inch pure platinum wire, 9 inches diameter by 12 inches high, is suspended. The gas passes into an aluminium head and down through the gauze.

The chief advantage of the cylindrical gauze, in addition to that of greater capacity per unit, is that heat is radiated from one part of the gauze to another, and it therefore operates at a higher temperature. This enables a higher conversion to be obtained, without the use of electrical heat.

The capacity of a square foot of gauze is approximately 2500 lbs. nitric acid per 24 hrs., or 350 lbs. nitric acid per oz. troy of platinum. For fuller details, references (The Oxidation of Ammonia Applied to Vitriol Chamber Plants, M.I.D. Research Laboratory, 1919; and Parsons, J. Ind. Eng. Chem. 1919, 11, 541–52) should be consulted. E. H. and F. C. Z.

NITROGEN, ATMOSPHERIC, UTILISATION OF. Nitrogenous substances, particularly nitrates and ammonium salts, are used as plant manures. The natural formation of combined nitrogen is insufficient to supply the soil, more particularly on account of wastage through the action of denitrifying bacteria, which yield free nitrogen, and from the present system of sewage disposal.

According to E. J. Russell (J. Soc. Chem. Ind. 1918, 37, 45R) one pound of combined nitrogen, properly used in the soil, will yield enough food to supply a man for about five days. Normally, a plant takes up practically the whole of its nitrogen in the form of nitrates, and the most efficient nitrogenous fertilisers are the nitrates of potassium, calcium, and sodium, probably in the order given. Other nitrogen compounds must first be oxidised to nitrates in the soil. Ammonia is rapidly oxidised to nitrates by soil bacteria, and ammonium salts applied to the soil are converted into nitrates before the plant is ready for all the nitrogen supplied. Protein nitrogen, amino-acid nitrogen, and amide-nitrogen, such as are present in farmyard manure, are also rapidly oxidised by soil bacteria. Calcium cyanamide is first converted into ammonia and then into nitrate in the soil. Other nitrogen compounds, such as diazo-compounds, nitro-compounds, and ring-compounds, are (as far as is known) useless as fertilisers. The relative values of combined nitrogen in various forms have been stated as follows: nitrate nitrogen, 100; ammonia nitrogen, 95; cyanamide nitrogen, 85–90 or more; protein nitrogen, 70–80.

The natural sources of combined nitrogen are twofold. First, electrical discharges in the atmosphere, cause the union of oxygen and nitrogen, with the ultimate production of nitrates and nitrites. (See, however, Moore, J. Chem. Soc. 1921, 119, 1555.) By this means it is estimated that every acre of ground in Great Britain is enriched annually to the extent of 11 lbs. of combined nitrogen. In the tropics, where thunderstorms are more frequent, the amount is larger.

The second natural source of combined nitrogen is the fixation of nitrogen by organisms in the soil. It is brought about by two groups of organisms. First, symbiotic organisms associated with living plants, especially those belonging to the pea family (leguminosæ), and occurring in nodules in the roots. These are now supposed to be bacilli, not pseudomoni, and are known as *B. radicicola*. Second, free-living micro-organisms in the soil, either aerobic (*Azotobacter chroococcum* and *A. agilis*), or anaerobic (*Clostridium pasteurianum*). The nitrification of ammonia by micro-organisms in the soil takes place normally in two stages. The oxidation to nitrous acid is brought about by two groups, viz. *nitrosomonas* and *nitrosococcus*. The final stage, in which nitrous is oxidised to nitric acid, is effected by *nitrobacter*. The actual products are, of course, salts of these acids, usually calcium salts. The direct oxidation of ammonia to nitric acid has been stated to occur as a result of the activity of Kaserer's bacillus (*B. nitrator*), but this lacks confirmation.

Denitrification, in which assimilable nitrogen compounds are decomposed with evolution of free nitrogen, is brought about by *B. denitrificans*, as well as by other groups of organisms (*B. stuzei*, &c.).

Attempts have often been made to use cultures of nitrogen-fixing bacteria in the soil for the purpose of promoting nitrification, under the names of 'nitragine,' 'nitrobacterine,' &c. These, and the use of 'bacterised peat,' do not appear to have been very satisfactory (*see* J. Soc. Chem. Ind. 1907, 26, 304).

Numerous experiments have been made with a view to the practical utilisation of the bacterial oxidation of ammonia to nitrates, notably by Muntz and Lainé, and Boulanger, of the Pasteur Institute, and by Lunden and Thorssell of Stockholm. The former used a mixture of charcoal, turf, and chalk, innoculated with nitrifying bacteria, through which a dilute solution of ammonium sulphate was percolated. The optimum temperature was found to be 30°C. The bacteria cannot tolerate too concentrated solutions of ammonium salts, but are unaffected by considerable amounts of nitrates. The liquor is therefore passed from one nitrifying bed to another, and enriched by the addition of a portion of ammonium sulphate between each bed and the next. A solution of calcium nitrate is obtained, which may be precipitated with ammonium carbonate to form ammonium nitrate. The highest concentration of calcium nitrate attained was 62·25 grams per litre; the nitrification then ceased. In semi-technical experiments the supply liquid contained 5·7 grams nitrogen as calcium nitrate, and 1·3 grams nitrogen as ammonia, per litre.

Lunden and Thorssell (Eng. Pats. 15667, 15668, 15670, and 15671, 1918) use a nutrient solution containing nitrates as well as ammonium salts; the latter may be ammonium nitrate, the ammonia of which is oxidised. After bacterial oxidation, part of the solution is used for the preparation of ammonium nitrate by adding ammonia and carbon dioxide; but the main part, enriched with more ammonium salt and a suitable amount of calcium carbonate, is sent back to the bacteria beds for further oxidation. Calcium carbonate or toilet sponge is used as substrate instead of turf, and a current of air passed through. The method of cultivating the bacteria (obtained from fertile soil) is described in Eng. Pat. 15669, 1918. Pure cultures are not essential, but extraneous organisms such as moulds and protozoa are injurious; they may be eliminated by avoiding organic matter in the culture media and by adding small amounts of poisons such as phenol, cuprous cyanide, sodium fluoride, and aniline, to which the nitrifying bacteria are very resistant.

The objections to such processes are their slowness, the space required for handling the enormous bulks of dilute solutions obtained, and the large amount of fuel required for evaporation.

The natural deposits of guano have long been exhausted, and the deposits of sodium nitrate of Chile are approaching a similar fate. If the improved processes for working these deposits are adopted (*see* SODIUM NITRATE), and are successful, the amount of workable nitre may amount to about 250,000,000 tons. At the present rate of consumption, this would extend the life of the beds to 100 years. Altogether, 200 years is believed to be a reasonable life if the deposits at present unworked are developed (Chimie et Industrie, March, 1920). These calculations, however, leave out of account the normal growth of demand, which is roughly doubled every ten years, and the cost of exploiting the poorer deposits will naturally rise, perhaps to a prohibitive limit in the face of competition with synthetic methods.

Next in importance to the Chilean deposits is ammonium sulphate, formerly exclusively and still largely obtained as a by-product in the manufacture of coal gas and metallurgical coke, during which processes only about 20 p.c. of the nitrogen of the coal is recovered as ammonia. In the Mond process of gasification, where large amounts of steam are passed along with air over the fuel, as much as 60 p.c. of the nitrogen is recovered, but all the other valuable by-products, such as benzene, are lost, and the gas is of relatively poor heating value. The supply of combined nitrogen obtainable in this way would, however, be entirely inadequate to meet the growing needs of agriculture.

The chief application of combined nitrogen is in the production of food. The exhaustion of the Chilean deposits without the possibility of alternative sources, would therefore give rise to what is known as the 'Nitrogen Problem,' *i.e.* the question of avoiding starvation.

Combined nitrogen also forms an essential constituent of large numbers of dyes, explosives, and drugs, and ammonia is used in the ammonia-soda process and in the liquid form in refrigeration. Cyanides are used in the extraction of gold and in electroplating. The peculiar urgency of the nitrogen problem under war conditions is clear.

The nitrogen of the atmosphere over every square mile of the earth amounts to about 20 million tons, or over thirty times the amount contained in the whole of the Chile nitre and by-product ammonium sulphate produced per annum. The supply is practically inexhaustible. The methods at present in use for fixing atmospheric nitrogen are as follows:—

1. The direct synthesis of ammonia from nitrogen and hydrogen gases (the Haber process): $N_2+3H_2 \rightleftarrows 2NH_3$.

2. The direct synthesis of nitric oxide from the air in the electric arc, followed by the conversion of this nitric acid and nitrates:

$$N_2+O_2 \rightleftarrows 2NO\ ;\ 2NO+H_2O+3O=2HNO_3.$$

3. The reaction between nitrogen and calcium carbide, leading to the production of calcium cyanamide, $CaCN_2$, which may be used directly as a fertiliser or decomposed by superheated water with production of ammonia:

$$CaC_2+N_2=CaCN_2+C\ ;$$
$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

4. The conversion of ammonia, obtained by method (1) or (3), into nitric acid and nitrates by catalytic oxidation:

$$4NH_3+5O_2=4NO+6H_2O.$$

Each method has particular advantages and disadvantages, depending mainly on the particular facilities offered by any locality in the way of cheap power, fuel, and skilled labour.

The enormous extension which has taken place in nitrogen fixation industries may be appreciated from the table at the top of the next page (Statistical Supplement to the Nitrogen Products Committee's Report, 1921), showing the actual output of fixed nitrogen in 1912 and the maximum potential capacity in 1920. The figures refer to world resources.

This table shows that whilst the relative output contributed by Chile has decreased to half, that of synthetic industries has increased from 4½ p.c. of the whole in 1912 to 43 p.c. in 1920. The most important fact is that *fixation processes are now the largest contributor to the world's requirements.* In spite of the enormous extensions of the Haber process, the cyanamide process is still the largest single contributor to the synthetic production of fixed nitrogen.

SYNTHETIC AMMONIA.

Experiments on the union of nitrogen and hydrogen, with formation of ammonia, on passing electric sparks through a mixture of the two gases, were made by Regnault in 1845, by Deville in 1865, and by H. B. Dixon in 1888

Source of supply	1912			1920		
	Output in long tons of product	Metric tons N	p.c. total output	Productive capacity in long tons of product	Metric tons N	p.c. total productive capacity
Chile nitrate industry (assuming 95 p.c. product) . .	2,586,975	411,329	57·5	2,966,061[1]	471,000	30·2
By-product Ammonium sulphate (24·5 p.c. ammonia assumed) . . .	1,229,773	272,007	38·0	2,015,440	413,000	26·6
Cyanamide (18 p.c. N).	126,538	22,435	3·1	1,777,000	325,000	20·9
Arc products (13 p.c. N). . . .	75,000	9,907	1·4	290,400	38,300	2·5
Synthetic ammonia .	nil	nil	nil	1,503,000	308,000	19·8
Total fixation . .	201,538	32,342	4·5	3,570,400	671,300	43·2
Grand total . .	4,018,286	715,678	100	8,551,900	1,555,300	100

(*see* also Briner and Mettler, J. Chim. Phys. 1908, 6, 137; Briner and Kahn, *ibid.* 1914, 12, 534; Briner and Baerfuss, Helvet chim. Acta, 1919, 2, 95, 162). Haber and van Oordt (Zeitsch. anorg. Chem. 1905, 44, 341) examined the production of ammonia on passing the mixed gas over iron, acting as a catalyst, at atmospheric pressure. An important advance was made by Nernst (Zeitsch. Elektrochem. 1907, 13, 521; 1910, 16, 96) and his assistant Jost (Zeitsch. anorg. Chem. 1908, 57, 414; Zeitsch. Elektrochem. 1908, 14, 373), who were the first to work under pressure (up to 30 atm.). Further investigations by Haber and his pupils (Haber and Le Rossignol, Zeitsch. Elektrochem. 1913, 19, 53; Haber, Ponnaz, and Tamaru, *ibid.* 1915, 21, 89; Haber and Maschke, *ibid.* 1915, 21, 128; Haber and Greenwood, *ibid.* 1915, 21, 241; *see* also Maxted, Ammonia and the Nitrides, 1921) led in 1910 to the adoption of the process by the Badische Co., in whose hands it has developed in a surprisingly short time into one of the greatest chemical industries in the world. In the perfecting of the technical details of the process Dr. C. Bosch took a leading part.

The Badische process consists in bringing a mixture of pure nitrogen and hydrogen, in the proportions of 1 to 3 by volume, under a pressure of 200 atm., in contact with a catalyst such as iron at about 600°. Under these conditions about 8 p.c. by volume of ammonia is produced when equilibrium is attained. The gases are circulated through the catalyst chamber by pumps and pass through a heat exchanger, in which they give up part of the heat evolved in the reaction to the incoming gases. The ammonia is removed from the gas by washing with water under high pressure and the residual gas again goes to the catalyst.

The reaction $N_2+3H_2 = 2NH_3$ is exothermic. The *heat of formation* of 1 gram mol. NH_3 at constant pressure is stated by Thomsen to be 11·89 kg. cal. at 18°C. Berthelot and Matignon at higher temperatures found 12·2 kg. cal. Nernst (Zeitsch. Elektrochem. 1910, 16, 96) calculates 15·1 kg. cal. at 850°. The heat of formation of ammonia was determined by Haber and Tamaru (Zeitsch. Elektrochem. 1915, 21, 191), and Haber, Tamaru, and Öholm (*ibid.* 206), whose results are summarised below:

t°C.	Q_p obs. (kg. cal.)	Q_p calc. (kg. cal.)
0	10·95	10·95
466	12·67	12·67
503	12·70	12·77
554	12·86	12·91
659	13·10	13 15

The values 'Q_p calc.' were found from the equation:

$$Q_p=10950+4{\cdot}5t-0{\cdot}001822t^2 \text{ gm. cal.}$$

The specific heat of ammonia was determined by Haber and Tamaru (Zeitsch. Elektrochem. 1915, 21, 228); for the true molecular heat at constant pressure they give:

$$C_p=8{\cdot}62+0{\cdot}0035t+5{\cdot}1\times10^{-6}t^2 \text{ gm. cal.}$$

Nernst's results are somewhat lower (Zeitsch. Elektrochem. 1910, 16, 96):

t°C.	C_p obs.	C_p calc	C_p obs. Nernst
309	10·3	10·2	9·45
422	11·0	11·0	10·0
523	11·8	11·8	10·7

Since the reaction is exothermic and occurs with diminution of volume, it is clear on thermodynamic grounds that the yield in equilibrium will be increased by working under high pressure at as low a temperature as is compatible with an adequate reaction velocity. Haber (Zeitsch. Elektrochem. 1914, 20, 597) gives the following yields, in percentages by volume, with the mixture N_2+3H_2. The whole of the results are represented by the equation:

$$\log K_p=2098/T-2{\cdot}5088\log T -0{\cdot}0001006T+0{\cdot}186\times10^{-6}T^2+2{\cdot}1$$

or, approximately: $\log K_p=2888\,T-6{\cdot}134$, where, in both cases, $K_p=P_{NH_3}/p^{\frac{3}{2}}_{H_2}p^{\frac{1}{2}}_{N_2}$.

(*See also* R. S. Tour, J. Ind. Eng. Chem. 1921, 13, 298.)

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[1] Maximum war output in 1917.

Temperature C.	Equilibrium percentage of ammonia (by vol.) 1 atm.	30 atm.	100 atm.	200 atm.	1000[1] atm.
200	15·3	67·6	80·6	85·8	—
300	2·18	31·8	52·1	62·8	—
400	0·44	10·7	25·1	36·3	—
500	0·129	3·62	10·4	17·6	—
536	—	—	—	—	40
600	0·049	1·43	4·47	8·25	—
607	—	—	—	—	30
672	—	—	—	—	20
700	0·0223	0·66	2·14	4·11	—
740	—	—	—	—	14
800	0·0117	0·35	1·15	2·24	—
900	0·0069	0·21	0·68	1·34	—
1000	0·0044	0·13	0·44	0·87	—

Lord Rayleigh, working with a mixture of nitrogen and hydrogen and an acid fountain in his apparatus (p. 581), observed that nitrogen was fixed as ammonia at about half the rate at which it was fixed as nitric oxide under the same conditions with oxygen. Maxted (J. Chem. Soc. 1918, 113, 168, 386; 1919, 115, 113; J. Soc. Chem. Ind. 1918, 37, 232T; Eng. Pats. 130023, 130063, 1919; *cf.* Briner, Helv. Chim. Acta, 1919, 2, 162) pointed out that the equation deduced from thermodynamics for the ammonia equilibrium would require a change of sign of the heat of formation of ammonia above 1000°C., and hence the yield of ammonia should increase with temperature at very high temperatures. This was confirmed experimentally by the formation of ammonia from nitrogen and hydrogen in the oxy-hydrogen blowpipe flame and in the arc. The highest percentage obtained at atmospheric pressure was 1·5. The possibility of synthesising ammonia in the arc at atmospheric pressure under conditions which do not require absolute purity of the gases may be kept in mind.

On account of the different compressibilities of nitrogen and hydrogen, a correction must be applied in making up the mixture by pumping one gas into a cylinder of the other to a given final pressure. This has been calculated by Cochrane (Physical and Chemical Data of Nitrogen Fixation, Munitions Inventions Department, Stationery Office, 1918).

The catalysts which bring about the union of hydrogen and nitrogen have been thoroughly investigated. Haber first used metallic osmium, but this is exceedingly expensive. He then found that uranium is nearly as effective as osmium. Crude uranium carbide obtained by the reduction of uranium oxide by carbon in the electric furnace is a convenient form. When brought in contact with nitrogen and hydrogen under pressure it absorbs nitrogen and falls to an extremely fine powder, which is very active.

In the later developments, in which pressures up to 200 atm. are used, iron has been found suitable. Nernst found that pure iron is relatively inactive. Its activity is considerably enhanced by the addition of other substances. Molybdenum and molybdic acid have also been found effective catalysts, after first being heated in a current of ammonia and changed into nitride.

Better yields are obtained by the addition of substances termed 'promoters' to iron, nickel, or cobalt used as the main catalytic agent. These substances are specified as compounds of magnesium, beryllium, aluminium, or of the alkali, alkaline-earth, or rare-earth metals, or of zirconium, vanadium, tantalum, chromium, manganese, molybdenum, or tungsten. Iron and molybdenum appear to form a very effective catalyst, although the physical properties of the catalyst, such as its tendency to disintegrate under pressure, must be carefully studied. The addition of the oxide or other compound of magnesium or aluminium is said to be particularly favourable. Certain substances diminish or destroy the catalytic property of the iron, &c. Such are, for example, arsenic, sulphur, selenium, tellurium, phosphorus, boron, antimony, bismuth, tin, lead, or zinc, or their compounds, and the presence of carbon monoxide and dioxide, and of oil, in the gases should be also be avoided. The reaction gases may be freed from contact poison by passing over a further quantity of the catalytic agent placed in advance. The mixture of iron and a promoter may be supported on a carrier, such as asbestos or fireclay, and one constituent of the carrier may constitute the promoter, but it is necessary in this case that the iron and promoter should be actually mixed together.

Deterioration of manganese used as a catalyst is prevented by the use of a mixture of nitrogen and hydrogen which has been freed from all traces of oxygen, by passage over metallic sodium, or manganese nitride or other substances that will decompose water and absorb oxygen, and they may be subjected to a preliminary treatment by passage over heated palladium asbestos and calcium chloride. The same precautions must be taken if manganese nitride is used.

The production of ammonia may be modified by passing nitrogen and hydrogen alternately over a catalyst, but this method does not seem to be in use.

The synthetic ammonia plant of the Badische Co. comprises two factories: the Oppau works, forming practically a continuation of the parent works at Ludwigshafen, and the Leuna works near Merseburg (Halle). Oppau, which is said to have cost £15,000,000, was commenced in 1913, with a capacity of 20 tons of NH_3 per day; during the war this was increased to 200 tons. The synthetic nitrogen products made at Oppau in 1918 are stated to have been:

	Tons per annum	NH_3 equivalent
Ammonium nitrate .	10,000	4,250
Sodium nitrate .	130,000	26,000
Nitric acid . . .	40,000	10,800
Ammonia liquor[1] .	—	40,000

A portion of the Oppau works was destroyed by an explosion in 1921 (*see* J. Soc. Chem. Ind. 1921, 40, 381R).

The Leuna works has been erected since 1916, and when completed, the output will be 800 tons daily of ammonia. The combined output of Oppau and Leuna has been given as follows (Statistical Supplement to Nitrogen

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[1] Results of Claude.

[1] Exported to Höchst for oxidation to nitric acid.

Products Committee Report, Stationery Office, 1921):—

Metric tons of ammonia per day.

	1914	1918	1920 (estd. max. capacity)
Oppau . .	25	220	250
Leuna . .	nil	400	800[1]
Total .	25	620	1050

Importation of Chile nitrate by Germany is no longer necessary. The German Minister of the Interior reported that Germany in 1916 made by all processes 400,000 tons of synthetic fixed nitrogen. Besides synthetic ammonia, other salts such as the chloride and nitrate and mixed salts for fertilisers are made at the Haber factories.

The power for both plants is cheaply produced from lignite, gasified in 'Bamag' producers, 12 feet by 25 feet, with rotary grates, a little steam being added to the air. In the Oppau works (to which the following description applies) the power plant generates 15,000–16,000 h.p. A row of 12 gas producers, each consuming 20 tons of lignite and yielding 2,000,000 cubic feet of gas per day, is built alongside a similar row of water-gas generators, which provide the hydrogen. The latter use Ruhr oven coke, and are of the Pintsch type with rotary grates, 15 feet by 25 feet, gasifying over 30 tons of coke to 3,000,000 cubic feet of gas each daily. Some air is added, and the resulting gas contains about 40 p.c. H_2, 30 p.c. CO, 12 p.c. CO_2, and ·18 p.c. N_2. The water gas is treated by the Bosch process (Eng. Pats. 26770, 1912; 27117, 1912; 124760, 1918; U.S. Pats. 1115776, 1914; 1200805, 1916; Zeitsch. kompr. und flüssige Gase, 1914, 16, 187), in which a mixture of water gas and steam is passed over a catalyst consisting of ferric oxide with promoters such as chromium oxide at a temperature of 400°–500° when the reaction $CO+H_2O \rightleftarrows CO_2+H_2$ takes place. The catalyst remains active for two years. The catalyst plant comprises 24 units in 2 sections of 2 rows of 6 or 7 units. Each unit has 2 heat exchangers and 1 elevated catalyst chamber; the latter is 16 feet by 12 feet by 10 feet deep, with an oval cover carrying two 8-inch pipes, and contains 2 trays of catalyst. The heat exchangers are 30 feet by 15 feet by 6 feet, and the whole apparatus is lagged, so that the reaction takes place without external heating. (The addition of a little oxygen or air to the gas has been described as a means of maintaining the temperature, a free flame burning in the catalyst chamber.) The gas issuing from the converters (in which the reaction is conducted at atmospheric pressure) contains a little CO (according to Greenwood, Industrial Gases, p. 163, this may be 2·5 p.c.) and must be purified from CO_2, residual CO and H_2S (from sulphur in the coke).

The purification (Eng. Pats. 9271 of 1914; 120546 of 1918; Fr. Pat. 389671 of 1908; U.S. Pat. 1196101 of 1916) is carried out by washing out the CO_2 with water under pressure (Eng. Pats. 11878 of 1910; 124761 of 1918); washing finally with soda (Eng. Pat. 15053 of 1914) is not used. Carbon monoxide is taken out by washing with ammoniacal copper formate solution and hot caustic soda solution under high pressure (Eng. Pat. 1759 of 1912; U.S. Pats. 1126371 of 1915; 1133087 of 1915; J. Amer. Chem. Soc. 1921, 43, 1) which also takes out H_2S. The copper solution contains excess of ammonia (not less than 6 p.c.) to prevent iron being attacked; the soda solution may contain 25 p.c. NaOH, and is brought in contact with the gas at 260° under 200 atm.

In the purification from carbon dioxide the gas, carried by a 3-feet main from the converters, is compressed to 25 atm. and passed to the bases of 8 steel towers, 30 feet by 4 feet, packed with rings, into the tops of which water at 25 atm. pressure is injected by circulating pumps. The water issues charged with CO_2; it is passed through Pelton wheels, in which 60 p.c. of the power is recovered, and the CO_2 evolved is collected. It is important that the amount of CO_2 recovered is more than sufficient to convert all the ammonia made into sulphate by the gypsum process, or into chloride by the ammonia-soda process (*see* below). The gas is now passed through steel bottles which act as spray catchers to the high-pressure plant. Here it is brought to 200 atm. and delivered to the carbon monoxide purifiers.

This plant consists of 16 towers of special steel, each in one piece, 25–30 feet high and 2 feet 6 inches external diameter, with flanged ends, and packed with Guttmann balls. In the first eight of these an ammoniacal copper formate solution is circulated, in the remainder caustic soda ($CO+NaOH=H{\cdot}COONa$). The liquids are circulated by 8 hydraulic pumps of forged steel, 200 h.p. total, and the ammoniacal copper solution, which absorbs ten times its volume of CO, is passed down a 40-feet tower, when the gas is released and collected. Spray traps in the form of vertical steel bottles are placed under these towers. The presence of 0·01 p.c. of CO in the final gas is said to be injurious.

The purified hydrogen (with some nitrogen from the air mixed in the water-gas operation) is now passed to the catalyst plant by a high-pressure main. The nitrogen content is brought up to the ratio $N_2 : 3H_2$ from a Linde plant and the gas is dried.

The catalyst plant in which the mixture is converted into ammonia consists of 15 steel bombs, each comprising two straight flanged sections, each 6 m. long and 80 cm. internal diameter, the walls being 18 cm. thick. These are bolted together and the covers are held on by fifteen 4-inch studs. The walls are perforated at intervals of 1 foot with $\frac{1}{4}$-inch tapering holes. Inside is a special steel liner, making a gas-tight joint with the ends (U.S. Pat. 1188530, 1916; D. R. PP. 254571 and 256236, 1911)—this is to prevent attack of the carbon-steel bomb by the hydrogen; a lining of electrolytic iron might also be possible. Inside this liner is probably a refractory lagging and a support for the catalyst, the internal diameter of the catalyst space being 50 cm. The outer walls are heavily lagged, and reach 300°–400°; the catalyst is at 600°. The temperature is maintained by heat exchangers, consisting of forged steel tubes, 6 m. long and 15 inches external diameter, fitted internally with nests of $\frac{5}{8}$-inch steel tubes autogenously welded into end plates. Each catalyst unit (costing 100,000 marks) is mounted vertically with its heat exchanger inside a brickwork compartment with strong iron doors and planking, with a little of the bomb projecting above. Starting is effected by adding oxygen (which does not come in contact with the catalyst) (D. R. P. 259870, 1911) or by electrical heating (U.S. Pat. 1202995, 1916). An iron catalyst with a promoter (possibly molybdenum) is used (D. R. P. 265295, 1912).

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[1] When complete; this capacity was not reached in 1920.

The gas is circulated through the catalyst; argon and methane may accumulate up to several p.c.; 10 p.c. of the gas is lost by leakage.

The ammonia is removed from the gas by solution in water under pressure (D. R. PP. 235421, 1908; 270192, 1912); liquefaction (U.S. Pat. 1202995, 1916) is not economical. Three water injector pumps are connected with 9 sets of absorbers, each consisting of 3 water-cooled steel spirals set vertically, the upper spiral being 60 feet above ground. The gas passes down the lowest spiral, rises to the top of the second spiral and passes down this, and similarly with the third spiral. Water flows down all the spirals by gravity. A solution containing 25 p.c. NH_3 is obtained. The gas is dried and sent back to the catalyst system.

The personnel at Oppau comprises 1500 labourers, 3000 mechanics, 350 clerks, and 350 chemists. The fuel requirements (McConnell, J. Ind. Eng. Chem. 1919, 11, 837) are 1750 tons of lignite (400 for gas engines, 1000 for steam for H_2 plant, and 350 for power plant), and 500 tons of coke (for H_2) per day. The daily cost of labour is £2,300, of fuel £2,300, and working expenses, interest, &c. £6700.

The Haber process carried out at Merseburg differs from that at Oppau in two respects: (1) the mixture of nitrogen and hydrogen is made directly by treating a mixture of producer (air) gas and water gas, with the addition of steam, by the Bosch process (Eng. Pat. 16209, 1920); (2) the purified mixture of nitrogen and hydrogen, before passing to the main catalyst furnaces, is passed through a series of small catalyst furnaces ('Vorofen') to remove impurities (Eng. Pat. 5835, 1911).

There are 31 gas generators, 5 for air gas and the rest for water gas, all the air being provided by two blowers, each of 350 h.p. The gases are passed through three gasholders, each of 1,765,000 cubic feet capacity, providing a reserve for fifteen minutes. From these the gases are taken and mixed by blowers. The mixed gas then takes up the requisite amount of water vapour in two rows of six towers, each 82 feet high, through which hot water is pumped by seven pumps, each of 70 h.p. The water is warmed in a tower by the gases leaving the heat exchanger of the contact furnaces for the hydrogen production. There are 48 heat exchanger towers.

The gases, containing hydrogen, nitrogen, carbon monoxide, steam and some carbon dioxide, now pass, after pre-heating, to two sets of 24 contact furnaces, in which the reaction $CO+H_2O \rightleftarrows CO_2+H_2$ occurs. The gas passes to two gasholders, one of 350,000 cubic feet and the other of 1,050,000 cubic feet capacity. Carbon dioxide is removed by washing in 21 to 30 towers at 25 atm., the compression of the gas being in large part effected by one of the cylinders of the 200 atm. compressors, although a few pumps for 25 atm. are provided. Pelton wheels recover about 40 p.c. of the energy of the released gas, which is utilised to compress the water to 25 atm. The power for this part of the plant is 40,000 h.p.

For the removal of the carbon monoxide, the gas compressed to 200 atm. by twenty-four 1000 h.p. compressors and twelve 500 h.p. compressors is scrubbed in 19 towers with ammoniacal copper formate solution circulated by 9 double pumps of 600 h.p. The carbon monoxide recovered by reducing the pressure in towers is sent along with water to the hydrogen contact plant. Six towers for caustic soda remove the remaining carbon monoxide, the soda being circulated by 6 small pumps.

The gas now passes to 9 small contact furnaces ('Vorofen'), in which the remaining impurities are removed by catalyst mass before passing to the main contact furnaces. There are 24 main catalyst furnaces (5 being in reserve), and 24 heat exchangers. Circulation is effected by 11 pumps of 700 h.p. each ('Umlaufpumpen'). The ammonia formed is absorbed in water, compressed to 200 atm. by five 100 h.p. and two 300 h.p. pumps in 20 towers 39·3 feet high and 29 inches diameter. The ammonia solution is passed to an expander, the ammonia gas evolved being absorbed in a separate tower. In the expansion the hydrogen and nitrogen gases dissolved in the water under 200 atm. pressure are liberated; these pass through the ammonia scrubbing tower and are collected in a gasholder, from which they re-enter the circulatory system.

The Badische Co. (D. R. P. 300724, 1920; *cf.* D. R. P. 299752, 1919) prepare synthetic ammonium sulphate by the interaction of a solution of ammonia in water, finely powdered gypsum, and carbon dioxide:

$$2NH_3+CO_2+CaSO_4+H_2O$$
$$=(NH_4)_2SO_4+CaCO_3(\text{ppd.})$$

(*see* also Wride, Chem. Age, 1920, 2, 32). They also prepare ammonium chloride, apparently by a modification of the ammonia-soda process (Zeitsch. angew. Chem. 1918, 31, 654), the salt being applicable as a fertiliser (Chem. Ind. 1919, 42, 438).

The only other synthetic ammonia factory outside Germany is the United States Nitrate Factory No. 1, at Sheffield, Alabama, erected during the war. This utilises the modified Haber process of the General Chemical Co. (U.S. Pats. 1141947–8, 1915; Eng. Pats. 120546, 1918; 124760–1–2, 1918). The catalyst is prepared by impregnating pumice with nickel or ferric nitrate, heating to 550°, reducing at this temperature with hydrogen, and treating with sodium and ammonia gas at 450°. Sodamide is formed in the spongy metal, and the mass acts at 500° under 70 atm (a much lower pressure than that used in Germany). The plant was designed to produce 21·5 tons of NH_3 daily, and cost 13,000,000 dollars, (Fairlie gives the cost as 20,000,000, other authorities as 14,000,000); the synthetic ammonia section cost 7,000,000 dollars but requires another million for completion. Three units are installed. The works was operated for a short time, but great difficulties were encountered owing to faulty design, and the works was closed in January, 1919, about three months after work began. The process developed into a straight blue water gas make, followed by addition of air in the hydrogen converters for flame combustion to maintain the temperature. Caustic scrubbing was discarded as giving too much sediment, and ammoniacal cuprous carbonate alone was used at low temperatures. The catalyst furnaces, which were operated at 100 atm., were similar to the well-known Badische converters for SO_3, but much thicker and capable of withstanding pressure. The catalyst was contained in the internal battery of iron tubes. Self-heating was not attained (R. S. Tour, J. Ind. Eng. Chem. 1920, 12, 844). The Haber process was investigated in England during the war by the Munitions Inventions Department, and a factory was begun at Billingham-on-Tees. The undertaking was acquired by Brunner, Mond and Co., who are understood to be erecting a factory for the production of 20 tons of ammonia per day, with possibility of extension. In France the process is to be worked by the Compagnie Nationale de l'Azote, under agreement with the Badische Co., and similar arrangements have been made in Italy and Japan. For post-war progress in nitrogen fixation *see* J. A. Harker, J. Soc. Chem. Ind 1922, 41, 387 R.

The Claude Process of Ammonia Synthesis.—The increased production of ammonia which would result from the use of very high pressures in the presence of catalysts is theoretically self-evident. The attainment of these very high pressures has been described by G. Claude (Eng. Pats. 130086, 1918; 140083, 140089, 142180, 150744, 153254, 1920; proposal to obtain hydrogen from coke-oven gas by removing methane by washing with a solvent, such as ether, at −50°C. under 100 atm. pressure, Eng. Pat. 130358, 1919; Compt. rend. 1921, 172, 974; production of hydrogen from water gas by partial liquefaction, Compt. rend. 1921, 173, 653). The increased evolution of heat consequent on the greater yield of ammonia has then to be eliminated (Eng. Pat. 150774, 1920; Compt. rend. 1922, 174, 157, 681). The gas after one passage over the catalyst at 900–1000 atm., which are the pressures specified, is so rich in ammonia (over 20 p.c. by vol.) that the latter may be liquefied out by water cooling, and the cold produced by the evaporation of the liquid ammonia utilised. A semi-technical Claude plant, dealing with 1 ton of gas per day, is in successful operation at Montereau, near Fontainebleau; the British rights have been acquired by the Cumberland Coal Power and Chemicals Co., who propose to erect a factory at Great Clifton, Cumberland, for the production of 50,000 tons of ammonium chloride per annum. It is proposed to combine the synthetic ammonia process with the Schreib modification of the ammonia-soda process (D. R. P. 36093, 1885; *see* Sodium Carbonate) for the production of ammonium chloride, but ammonium sulphate will also be manufactured (J. Soc. Chem. Ind. 1921, 40, 420R).

Fixation of Nitrogen as Nitrides.

Many elements such as lithium, calcium, magnesium, and boron absorb nitrogen when heated, forming nitrides, *e.g.* Li_3N and Ca_3N_2, which are decomposed by water with evolution of ammonia: $Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$ (*see* Maxted, Ammonia and the Nitrides, 1921). Owing to the difficulty of reducing the hydroxides to metals the use of such substances as intermediaries in a continuous process for the fixation of atmospheric nitrogen has not found industrial application. A more promising reaction is the formation of aluminium nitride, AlN, from nitrogen and a mixture of alumina and carbon at very high temperatures:

$$Al_2O_3+3C+N_2 \rightleftarrows 2AlN+3CO-213{\cdot}2 \text{ kg. cal.}$$

Aluminium itself begins to absorb nitrogen at 750° (Fichter and Oesterheld, Zeitsch. Elektrochem. 1915, 21, 50) Aluminium nitride can be decomposed by heating with water and a little alkali under pressure, with the production of alumina, which may serve for the manufacture of metallic aluminium: $AlN+3H_2O=Al(OH)_3+NH_3$.

These reactions were applied in the Serpek process (Eng. Pat. 13086, 1910, and numerous later patents), which was worked for a time in the Savoy, but later abandoned. The absorption was found to be greatly accelerated by the presence of iron oxide, so that bauxite forms a suitable raw material. The mixture of bauxite and coke was heated in a stream of producer gas in a revolving tube furnace in the walls of which were embedded carbon rods carrying an electric current to heat the mass. A temperature of 1800°C. was necessary and the refractories suffered considerably. The original claim was 1 kg. N fixed for 10–12 kw. hr., a very attractive figure. The residue after decomposition could be used for the manufacture of aluminium.

Experiments were conducted by the Aluminium Co. of America, with the object of finding a suitable refractory. Serpek states that a mixture of hydrogen and nitrogen gives better results than producer gas in the revolving furnace. In the latest type of furnace (Zeitsch. komprimierte u. flüss. Gase, 1914, 16, 55) rotation is abandoned and a short chamber, 4 m. high and 1·5 m. wide, is used. The mixture of bauxite and carbon is dropped through the nitrogen at a temperature not exceeding 1250°–1300°, and conversion takes place more rapidly than the 5 to 6 hours' contact required in the revolving furnace. It is said that addition of hydrogen to the gases is not essential; producer gas is used and pure carbon monoxide passes out of the furnace. Two tons of alumina are obtained and 500 kg. nitrogen fixed per h.p. year. The process does not appear to be used on the industrial scale. (*See* also Escher, Chem. Zeit. 1918, 42, 353, 361; Shoeld, U.S. Pat. 1344153, 1920; Herman, D. R. P. 319046, 1920.)

Fixation of Nitrogen as Cyanides.

Dawes, in 1835, found that cyanides are produced in the blast furnace, and the researches of Bunsen and Playfair (B. A. Rep. 1845) showed that these cyanides are formed by the interaction of atmospheric nitrogen with potassium and carbon compounds in the furnace. Lewis Thompson, in 1839, found that when nitrogen is passed over a mixture of potassium carbonate and carbon at a high temperature, potassium cyanide is formed; with sodium carbonate the yield is very small. The process was used on a small scale at Grenelle (Possoz and Boissiere, Fr. Pat. 12205, 1842) and at Newcastle-on-Tyne, but owing to the intense action of the materials on the furnaces the method was discontinued. In 1860 Margueritte and de Sourdeval (Eng. Pats. 1027, 1172, 1860; *cf.* D. R. PP. 190955, 197394, 1906) found that barium hydroxide or carbonate gives better results than potassium compounds. Barium cyanide is formed which may be decomposed with steam at 300° with evolution of ammonia :

$$Ba(CN)_2+4H_2O=Ba(OH)_2+2NH_3+2CO.$$

The process was worked, with improvements, by Mond (U.S. Pat. 269309, 1882), but ultimately abandoned. Readman used the same process, with electrical heating, between 1899 and 1907, at the works of the Scottish Cyanides Co., and experiments are at present being carried out at Birmingham on the process.

A new impetus was given to the cyanide process by the publication by J. E. Bucher (J. Ind. Eng. Chem. 1917, 9, 233) of the claim that nitrogen can be economically fixed as sodium cyanide by heating an intimate mixture of equal weights of sodium carbonate, finely ground charcoal, and metallic iron at 950° in a current of nitrogen :

$$Na_2CO_3+4C+N_2=2NaCN+3CO-138{\cdot}5 \text{ kg.cal.}$$

Later experiments indicate that above a temperature of 1080° the cyanide decomposes. The resulting product was said by Bucher to contain 20–30 p.c. of sodium cyanide, or 5·7–8·7 p.c. of nitrogen. It may be decomposed by heating in steam with formation of ammonia and sodium formate :

$$NaCN+2H_2O=H{\cdot}CO_2Na+NH_3$$

All the essential features of Bucher's process had been patented by Adler in 1881 (D. R. P. 12351), but the rights were allowed to lapse. The process was investigated on a technical scale by the U.S. Government at Saltville, Va., and by the Air Reduction Co. (J. Ind. Eng. Chem. 1919, 1010 ; Met. and Chem. Eng. 1920, 22, 313). The U.S. Government plant at Saltville was ready for operation at the armistice. A mixture of sodium carbonate, carbon and powdered iron was externally heated in iron tubes at 1000°C. The product was extracted with anhydrous liquid ammonia, which dissolves only NaCN. The product contained 92 p.c. NaCN (*see* Brown, J. Ind. Eng. Chem. 1919, 1010 ; U.S. Pats. 1313313 and 1314236 ; Hara and Hayashi, J. Chem. Ind. Tokyo, 1919, 22, 175 ; Clancy, U.S. Pat. 1329652 ; Met. and Chem. Eng 1920, 92, 856). G. W. Heise and H. E. Foote (J. Ind. Eng. Chem. 1920, 12, 331) describe the production of ammonia and formates from cyanides. Poor results were obtained by heating Bucher briquettes in steam at 50 lb. pressure, hydrogen and ferrocyanides being formed. Under 300 lb. pressure, 92·5 p.c. of the ammonia was evolved ; at 120–130 lb. pressure 68 p.c. of the ammonia was evolved, together with some hydrogen. C. F. Bierbauer and L. S. Finch (U.S. Pats. 1295262 and 1295293, 1918) dissolve the crude cyanide as rapidly as possible by blowing the pulverised briquettes into a tank equipped with a water spray and agitator, filter rapidly and heat the solution with steam under 125 lb. pressure, the ammonia being allowed to escape through a release valve set at 50 lb. pressure. If the briquettes could be steamed without disintegration they could be put back into the retorts three times unless the formates and oxalates are to be recovered. Barium compounds might be preferable to sodium, it is stated. With steam at atmospheric pressure a temperature of 600° is required for good results ; at 100 lb. pressure, 400° is sufficient. There are no indications of side reactions, ammonia and formate being the only products. F. T. Metzger (U.S. Pat. 1313312 and 1313313, 1919) extracts formates from the residue with aqueous ethyl or methyl alcohol (20–80 p.c. alcohol). Cyanides may be extracted with aqueous acetone. Mount (U.S. Pat. 1329721 ; Met. and Chem. Eng. 1920, 22, 709) uses a continuous process ; Thompson (*ibid.* 1922, 26, 124) states that a pure form of carbon is necessary.

The production of hydrocyanic acid by striking a carbon arc in a mixture of hydrogen and nitrogen was observed by Dewar in 1879 (Chem. News, 39, 282). Gruskiewicz (Zeitsch. Elektrochem. 1903, 9, 83) obtained HCN from CO, H_2, and N_2 in contact with the arc. The reaction was investigated by Smith and Hutton (Tr. Amer. Electrochem. Soc. 1908). The reaction $N_2+H_2+2C \rightleftarrows 2HCN$ begins at 1800° and increases rapidly with temperature. Good results are obtained with mixtures containing CO, and with producer gas (*see* Diffenbach and Moldenhauer, D. R. P. 228539 ; Consortium für Elektrochemische Industrie, D. R. PP. 263692 and 268277). Lipinski (Zeitsch. Elektrochem. 1911, 17, 761 ; Moscicki, *ibid.* 877) produces HCN from methane, hydrogen, and nitrogen in the electric arc. In 1914 the process was in operation on a technical scale at Neuhausen in Switzerland. The conversion was said to be quantitative : $2CH_4+N_2=2HCN+3H_2$ The best results were obtained with a mixture containing 5–10 p.c. of methane, 13–24 p.c. of nitrogen, and 66–81 p.c. of hydrogen. A yield of 30 gram HCN per kw. hr. was claimed. The chief difficulty was the deposition of graphitoidal carbon on the electrodes. Briner and Baerfuss (Helvet. chim. Acta, 1919, 2, 663) obtained the highest yields under low pressure with excess of nitrogen. The maximum yield was 7·4 gram HCN and 0·5 gram NH_3 per kw. hr. with CH_4+5N_2 at 100 mm. pressure. P. A. Starke (U.S. Pat. 1306862) reduced the temperature by passing the gas over a catalytic mass of iron, nickel, cobalt, and an alkaline earth oxide at 800°–1000° without an arc. Lipinski uses metallic vapours and $CaCl_2$ vapour in the arc for increasing the yield.

The Cyanamide Process.—The synthesis of hydrocyanic acid was effected in 1868 by Berthelot (Compt rend. 1868, 67, 1141), who passed an electric arc through a mixture of acetylene and nitrogen : $C_2H_2+N_2=2HCN$. Berthelot expressed the opinion that cyanides could be prepared by the action of nitrogen on carbides at high temperatures. Although cyanogen has been detected in the spectrum of a carbon arc in nitrogen, the gas could not be isolated on account of its instability (Wartenberg, Zeitsch. anorg. Chem. 1907, 52, 299). In 1894 Moissan found that calcium carbide could be prepared by heating a mixture of lime and carbon in the electric furnace. In the pure state, according to Moissan (Compt. rend. 1894, 118, 501) calcium carbide does not absorb nitrogen at 1200°C. F. Rothe, working with crude carbide, found that absorption of nitrogen occurred readily at that temperature, but the product is not calcium cyanide but a mixture of calcium cyanamide and graphite:

$$CaC_2+N_2=CaCN_2+C$$

This discovery was patented by Frank and Caro, who are usually given the credit for the cyanamide process (Zeitsch. angew. Chem. 1906, 19, 835; *ibid.* 1909, 22, 1178). If the mixture so obtained is fused with sodium carbonate or chloride, sodium cyanide is formed:

$$CaCN_2+C+Na_2CO_3=CaCO_3+2NaCN$$

If barium carbide is used instead of calcium carbide, 30 p.c. of the nitrogen is absorbed as barium cyanide and the rest as barium cyanamide (Erlwein, Zeitsch. angew. Chem. 1903, 533). Cyanides were made by this process by the Frankfurt Gold- und Silber-scheideanstalt, the Deutsche Bank, and Siemens and Halske. On heating calcium cyanamide with water in an autoclave, or with superheated steam, ammonia is evolved: $CaCN_2+3H_2O=CaCO_3+2NH_3$. The raw, dark-grey product obtained by the absorption of nitrogen by calcium carbide is known as 'nitrolim,' or 'Kalkstickstoff.' It contains about 20 p.c. of combined nitrogen. When treated with water to remove unchanged carbide, the product is known as 'cyanamide,' and is used as a fertiliser.

The production of calcium cyanamide is shown in the following table, taken from the Statistical Supplement to the Report of the Nitrogen Products Committee, 1921.

METRIC TONS OF CALCIUM CYANAMIDE.

Country	1913	1914	1915	1916	1917	1918	1919
Germany	48,500	66,000	73,700	170,920 [2]	183,100 [2]	178,000	—
Austria-Hungary	7,500	(24,000)	(24,000)	(24,000)	24,000	24,000	—
France	7,500	(7,500)	(80,000)	(100,000)	100,000	100,000	—
Italy	14,982	15,556	25,292	25,105	12,300	15,000	—
Norway	22,110	14,670	25,000	26,409	182,387	178,472	—
Sweden	18,352	18,000	16,363	18,000	17,613	21,528	—
Switzerland	7,500	(7,500)	(12,500)	(29,500)	40,000	40,000	—
Canada [1]	48,000	(58,000)	(58,000)	(58,000)	58,000	58,000	65,317
United States	—	—	—	—	—	3,000 [3]	3,500 [3]
Japan	7,000	11,171	30,278	33,462	50,802	50,802	—
	181,444	222,397	345,133	485,396	668,202	668,802	68,817
Equivalent combined nitrogen on basis of nitrogen content of 18 p.c.	32,660	40,031	62,124	87,371	120,276	120,384	12,387

Brackets indicate productive capacity rather than actual output.

Pure calcium cyanamide is obtained by heating dicyandiamide with calcium oxide at 900°-1000°C. in nitrogen gas (Kameyama, J. Coll. Eng. Tokyo, 1920, 10, 173). The formation of cyanamide has been studied by M. de K. Thompson and R. H. Lombard (Met. and Chem. Eng. 1910, 617, 682), who found that the system comprised of CaC_2, $CaCN_2$, C, and N_2 is monovariant, *i.e.* there is at every temperature a fixed pressure of nitrogen in equilibrium, and this pressure is very approximately a linear function of the temperature between 1050° and 1450°C. Le Blanc and Eschmann (Zeitsch. Elektrochem. 1911, 17, 20), on the other hand, find that the pressure depends on the nitrogen content of the solid phase as well as on the temperature, which indicates that solid solutions are formed. Other things being constant, the rate of absorption is proportional to the pressure (Bredig, Fraenkel, and Wilke, Zeitsch. Elektrochem. 1907, 13, 69, 605). The action of fluxes, *e.g.* calcium fluoride, in the formation of cyanamide has been studied by the last-named authors, by Foerster and Jacoby (*ibid.* 1907, 13, 101; 1909, 15, 820), and by Polzenius (D. R. P. 163320). Calcium chloride lowers the temperature of absorption of nitrogen from 1100°C. to about 800°C., calcium fluoride to 900°C. The action of the fluxes is supposed to be the removal of a protecting film from the surface of the carbide.

The heat of reaction per mol. of carbide, $CaC_2+N_2=CaCN_2+C$ (graphite), has been calculated by Matignon (Ann. Chim. 1908, 14, 51) as 43·75 kg. cal., and by Dolch (Zeitsch. Elektrochem. 1920, 26, 455) as 58·7 kg. cal. By measurement of the heat of combustion of pure calcium cyanamide. N. Kameyama (J. Coll. Eng. Tokyo, 1920, 10, 173, 249) finds the heat of reaction to be 74·99 kg. cal., or 2·78 kg. cal. per gram of nitrogen fixed. The heat of formation of calcium cyanamide from its elements he calculates as 94·82 kg. cal. (amorphous carbon). The heat evolved in the formation of ammonia from cyanamide he gives as:

$$CaCN_2+3H_2O\ (\text{liquid}) =CaCO_3(\text{calcite})+2NH_3(\text{gas})+14{\cdot}13\ \text{kg. cal.}$$

This gives 415 C.H.U. evolved per lb. of ammonia; Landis estimates this at 200–300 C.H.U. in the autoclaves.

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[1] Works owned by American Cyanamide Co.
[2] Probably does not include cyanamide used as a source of ammonia for munition purposes.
[3] Production commenced just prior to the armistice.

The processes in use for the absorption of nitrogen by calcium carbide may be divided into three groups: (1) those in which externally-fired retorts are used, and the process worked discontinuously; (2) those in which the carbide is heated by electricity passed through a carbon rod in the mass of carbide, the process being worked discontinuously; (3) those in which the carbide is passed continuously through an electric furnace in a current of nitrogen.

The overall power requirement for cyanamide production, including carbide, is 2·3 kw. yr. (of 8500 hr.) per metric ton N fixed; or, as 0·5 kw. yr. is required per ton of carbide, and 4 tons of carbide are required to fix 1 ton of nitrogen as cyanamide, the power required for conversion of carbide to cyanamide alone is 0·3 kw. yr. per metric ton N fixed.

Calcium cyanamide was first made in 1905 on a technical scale at Piano d'Orte, in Italy (Zeitsch. Elektrochem. 1906, 12, 551). The manufacture of cyanamide at Odda, Norway, was begun by the erection in 1908 by the Alby Carbide Factories, Ltd., of a carbide factory for a yearly output of 32,000 tons of carbide, together with the erection of an adjacent factory by the North Western Cyanamide Co. for the production of 12,000 tons of calcium cyanamide per annum. Later, a cyanamide works was erected at Odda for the production of 16,000 tons per annum. The name of the Alby Carbide Co. was then changed to the Nitrogen Products and Carbide Co. (Zeit. für komprimiert. und flüssige Gase, 1916, 18, 168). The production at Odda is given as follows:—

	Carbide made per annum in tons	Carbide used for cyanamide per annum in tons
1908-1912 .	32,000	10,000 (15,000 kw. power used)
1912 . .	85,000	57,000 (37,000 kw. used; 4500 for motors)

The carbide factory uses yearly 150,000 tons of Norwegian limestone, 50,000 tons of English anthracite, and 15,000 tons of English gas-coke. The nitrogen is obtained from a Linde apparatus in 7 units, producing 2830 cu. m. of nitrogen per hour (each unit 100,000 cubic feet per hour), and dealing with 100 tons of liquid air per day. In the cyanamide furnace house there are about 600 furnaces, composed of cylindrical steel rings lined with refractory brick and lagged outside. Each furnace takes 450 kgm. of carbide in an inner retort. A carbon rod passes down the centre of the carbide and each furnace has a separate nitrogen gas connection. The furnace is closed at the top, heated to 1100°-1200°, and nitrogen passed in. Sintering occurs and the charge shrinks from the retort. The nitrogen penetrates to the centre of the charge through cracks in the mass, and the charge is converted from the outside to the centre in about 30 hours. The retorts are then taken out of the furnaces and sent to a cooling room in which are two large fans. The cyanamide is tipped out and crushed. The crushed material is sent to a silo of 7000 tons or to the hydrating and oiling plant. In this it is mixed with water mechanically and the mass, which becomes heated, is passed through a rotating tube for cooling. The dry powder is then mixed in mills with oil and packed in bags.

About 1·7 tons of limestone and 0·2–0·3 ton of ordinary coal are required to produce enough lime for a ton of carbide. About 0·62 ton of anthracite are required, with the lime, for this purpose. The consumption of electrodes amounts to about 0·025 ton per ton of carbide. The reaction $CaO+3C=CaC_2+CO$ is endothermic, requiring in practice about 0·5 kw. year per ton of carbide. A capacity of 20,000 tons of carbide per annum is regarded as the minimum economic capacity of a single carbide furnace. The nitrogen from the Linde apparatus at Odda contains less than 0·4 p.c. of oxygen. In the new Alby works a Claude apparatus is installed, the nitrogen from which is said to contain less than 0·2 p.c. of oxygen. The energy consumption is about 0·4 kw. hr. per cu. m. N_2 in the Linde, and somewhat less in the Claude plant. The Alby Carbide Factories, Ltd., was in liquidation in 1922.

In part of the Niagara works the nitrogen is produced by passing air over red-hot copper, the oxide formed being reduced by coal gas rich in hydrogen from the coking plant used in connection with the carbide furnaces. The new plant at Niagara uses liquid air. The presence of oxygen, moisture, carbon dioxide, and carbon monoxide in the nitrogen is deleterious, on account of the following side reactions in the preparation of cyanamide:

(1) $CaC_2+2H_2O=Ca(OH)_2+C_2H_2$
(2) $CaC_2+CO=CaO+3C$
(3) $2CaC_2+CO_2=2CaO+5C$
(4) $CaC_2+2O_2=CaCO_3+CO$.

The Muscle Shoals Nitrate Plant (A. M. Fairlie, Met. and Chem. Eng. 1919, 20, 8; C. Jones, *ibid.* 1920, 22, 182) is the largest cyanamide factory in the world. Cyanamide had been made since 1909 at Niagara (Landis, J. Ind. Eng. Chem. 1916, 8, 156), and at the outbreak of war this plant had a capacity of 64,000 tons per annum. Late in 1917 the American Cyanamid Co. formed a subsidiary company, the Air Nitrates Corporation, to erect the U.S. Nitrate Plant No. 2 at Muscle Shoals, Alabama, for a capacity of 110,000 tons of ammonium nitrate per annum. Plants 3 and 4 at Toledo and Cincinnati, respectively, were completed as buildings only at the time of the armistice.

In the construction of Plant 2 at Muscle Shoals, which is said to have cost £12,000,000, 20,000 men were employed on a site of 2200 acres, a town of 12,000 people coming into being. When operating at full capacity the plant employs 3000-4000 men. Muscle Shoals is on the Tennessee River, between Sheffield and Florence. The parts of the plant comprise: (1) the Power Plant; (2) the Carbide Materials department; (3) the Carbide Furnaces department; (4) the Carbide Mill department; (5) the Nitrogen department; (6) the Cyanamide department; (7) the Cyanamide Mills; (8) the Ammonia Gas department; (9) the Nitric Acid department; (10) the Ammonium Nitrate department. All these are laid out in order from north to south, except the nitrogen plant, which is placed far to the east to avoid contamination of the air used with gases from the other parts of the plant.

The power plant will ultimately be hydro-electric (Chem. and Met. Eng. 1920, 22, 417). The present scheme of 90,000 kw. is partly generated by a steam power plant of 60,000 kw. at the works, and partly supplied (30,000 kw.) by the Alabama Power Co. from a steam plant at the Government-owned extension of the Warrior River power plant on the Alabama coal-fields at Gorgas and transmitted 88 miles. At Muscle Shoals Westinghouse turbines and generators, 60-cycle, 3-phase, 12,200 volts are used, the power being transmitted through a brick and concrete bus tunnel 8 feet high, and 3600 feet long. The erection of a dam at Warrior River for hydro-electric power is now proceeding, and completion is expected in 1922 at a cost of over £4,000,000. The works itself cost £20,000,000.

The Carbide Section. Limestone crushed to ½–2 inches from Government quarries 20 miles distant is discharged from cars at the north end of the limestone kiln building by dumping from drop-bottom cars or with a crane. It is carried by a conveyor belt to a bucket elevator, hoisted to the upper floor and distributed by a conveyor belt among 7 concrete silos each of 6000 cubic feet capacity. A typical analysis is: SiO_2, 0·49; Al_2O_3 and Fe_2O_3, 0·30; $CaCO_3$, 98·23; $MgCO_3$, 0 97; moisture and loss at 175°C., 0·07. The stone is fed to the kilns by a cradle-feeding device. There are 7 rotary kilns, 8 feet diameter and 125 feet long, nearly horizontal (5 feet in 125 feet) steel shells lined with firebrick and rotated at ½ r.p.m. by bevel gears. The stone is fed into the upper end and fired at the lower end by powdered coal and air blast. The temperature reaches 760°–1090°C. and the process is continuous, 3 to 4 hours being required. The capacity of each kiln is 200 tons raw stone per day. The quicklime is discharged into 7 horizontal cooling kilns, 5 feet diameter and 50 feet long, turning 3 r.p.m. The cooled lime is then sent to the raw materials building.

The coal-mill building, situated alongside, comprises a bin, crusher, silo, and drier. The dried coal is fed to 4 Fuller pulverising mills, and is elevated to steel silos opposite each lime-kiln, from which it is fed by the air blasts.

In the coke drier building the coke is crushed, screened, and dried in coal-fired rotary driers. It is then conveyed to 8 silos in the raw materials building for use in the carbide furnaces. In this building the coke and quicklime are weighed by two Schaffer poidometers beneath the two bins, operating continuously and set to weigh out exactly the right amounts of coke and lime, which are then delivered to a conveyor belt and transferred to the carbide room. The mixed charge is distributed to 24 steel silos in the furnace house.

There are 12 rectangular carbide furnaces, 2 spare, each 12 feet by 22 feet by 6 feet inside, composed of steel boxes open at the top and lined with firebrick. The electrodes are assembled in a separate room and are 16 inches square and 6 feet 5 inches long. A copper head is bolted on one end, three electrodes are fastened together as a unit, covered with wire netting and pasted with asbestos and retort cement, afterwards baked in an electric furnace. Each assembled electrode weighs 7000 lbs. The heads are water-cooled. Three complete assembled electrodes are suspended over the top of the furnace. The depth of immersion is controlled automatically at the switchboard. The bus bars are five-sixteenth inch thick and 8 inches wide, and there are 16 bars to each electrode. The voltage for the carbide furnaces is 130, steppe down from 12,000 by transformers. There is one bank of transformers per furnace, each of 8325 kw. The current is 20,000 amp., the normal capacity of a furnace 48 tons of carbide per day of 24 hours. The temperature is 3000°C., the power consumption 124 kw. days per ton of 80 p.c. carbide, the electrode consumption 50 lbs. per ton of carbide. Carbon monoxide burns at the top of the furnaces. At the bottom of the furnace is one layer of graphite electrodes 16 inches square and 48 inches long, and a layer of tar and gravel on the top. In starting a layer of coke is thrown in, then a charge of 100 parts of lime to 600–620 parts of coke, previously mixed as described. This is shovelled from the floor until the furnace is full. The first tap of carbide is made 6 hours from starting and then the furnace is tapped every 45 minutes, the charge being renewed the whole time. The furnace is tapped by burning out the tapping hole with a portable electrode, and the molten carbide flows into chill cars of ½-ton capacity. After tapping, the hole is stopped by throwing a few shovelfuls of powdered carbide at the outlet, when the outflowing mass soon solidifies. The chill cars are hauled by electric locomotives to the carbide cooling house.

In the carbide mills, the carbide pigs are picked off the cars by cranes and set aside. Considerable shrinkage occurs and the blocks when sufficiently cool are dumped on to the crusher platform. The average composition is:

CaC_2	82·30	p.c.	Ca_3P_2	0·07	p.c.
C	1·20	,,	CaS	0·13	,,
CaO	14·72	,,	FeSi	0·72	,,
CaSi	0·06	,,	Undetermined	0·80	,,

There are three crushers reducing to 1¼ inch, and three mills (1 spare) grinding to pass 80 p.c. through 40-mesh screen and the rest through 10-mesh screen. There are then three tube mills pulverising, so that 85 p.c. will pass through 200-mesh screen. Each unit deals with 15 tons per hour. All these operations are done in an atmosphere of nitrogen to prevent explosions. The milled carbide is conveyed to 8 silos in the cyanamide building.

The Nitrogen Plant. The intakes are two 36-inch pipes extending north and south from the building. The air is drawn in by Root cycloidal blowers and sent through 16 scrubbing towers, 8 feet diameter and 30 feet high, packed with 6-inch spiral rings and fed with 17°Bé. caustic soda to remove carbon dioxide.

The nitrogen plant is of the Claude system. There are 15 compressor units furnishing air at 600 lbs. pressure to 30 nitrogen columns. The compression is done in three stages, 30 lbs., 140 lbs., and 600 lbs. Six columns are spare. The columns are oval in shape, 4½ feet diameter and 24 feet high. The rectifier consists of a series of superposed horizontal trays each 1½ inch deep with a layer of liquid resting on it. The compressed air expands from 600 lbs to 50 lbs., operating a small engine giving 4 to 5 h.p. to waste, and enters the rectifier below the critical temperature. A small part of the air at 600 lbs. is admitted and the pressure liquefies the air. The liquid, containing 45-50 p.c. of oxygen, goes to the bottom of the column, and after spraying with liquid nitrogen the gas escaping at the top is 99·9 p.c. nitrogen. This gas is passed through two heat exchangers to a 30-inch main to the cyanamide building. It escapes from the rectifier under a pressure of 10 inches of water and goes to the building at 4 inches. Each column produces 500 cu m. of nitrogen per hour. (The largest Linde machine produces 1000 cu. m.) The oxygen is allowed to escape to waste (*see* p. 598).

The Cynamide Furnace Department. There are 16 rows of furnaces, 96 in each row, or 1536 in all. Of these 1500 are in operation. These rows are in two sets, one on each side of a central gangway in the building. In this gangway the paper liners are made. The furnaces are 4 feet 4 inches outside diameter and 2 feet 10 inches inside diameter, and 5 feet 4 inches deep. They are steel shells with 9-inch firebrick lining. To charge a furnace a cylindrical paper tube container 2 feet 6 inches diameter with a vertical paper tube 3 inches diameter in the centre is inserted into the cold furnace and a charge of 1600 lbs. of milled carbide put in. There is an annular space of 2 inches between the paper and furnace wall. The carbon electrode is a ⅝-inch pencil, 6 feet 6 inches long, inserted in the paper tube. The covers are put on and the outer cover luted with sand.

The nitrogen is brought in by an 8-inch pipe between each pair of furnaces and two 1½-inch pipes carry off to the furnace, one to the bottom at the centre and the other at the side 6 inches above the bottom, each provided with a valve. The nitrogen reaches the furnace under a pressure of 3-4 inches of water.

Single phase current of 100 volts and 200–250 amps. is turned on through the carbon rod for 20 minutes, and is then cut down to 50 volts and 100–115 amps. for 12 hours. The reaction gives out heat and is allowed to continue without current for 28 hours altogether. The temperature in the furnace is about 1100°C.; the material does not melt but sinters into a solid cake. The product contains about 63 p.c. $CaCN_2$, 2 p.c. CaC_2, 13 p.c. CaO, and 11 p.c. C. The finished material is conveyed to a mill which is an exact duplicate of the carbide mill. It is pulverised so that 95 p.c. passes 200 mesh, all in an atmosphere of nitrogen. The milled material is fed at a controlled rate to the hydrating troughs, of which there are three, 36 feet long and 3 feet diameter, each containing a horizontal shaft with projecting arms 20 inches long. Water is sprayed in at the feed end at a calculated rate to decompose the unchanged carbide. The material at the exit must be perfectly dry. The agitator rotates at 50 r.p.m. and conveys the material at the rate of 50 feet per minute. The cyanamide is conveyed through an overhead tunnel to the ammonia autoclave building 300 feet away.

This contains 56 autoclaves in 7 units, one spare, rated at 100 tons per unit per day. They are of steel and cylindrical, 8 feet diameter and 20 feet high, each provided with a vertical agitator revolving 12 times per minute. A 2 p.c. solution of caustic soda is run in to a depth of 9 feet and 300 lbs. of soda ash added, which reacts with the 13 p.c. of free lime in the cyanamide to form caustic soda of about 3 p.c. strength. The charge of 8000 lbs. of cyanamide is added from weigh bins. The acetylene from the 2 p.c. still undecomposed carbide is allowed to escape through one valve through an exhaust fan. The outlet pipe is then tightly closed and steam from special boilers admitted at 150 lbs. for 20 minutes. Ammonia forms, the reaction being exothermic. When the pressure reaches 250 lbs. the ammonia valve is opened cautiously, but the pressure is maintained for 3 hours. The pressure then falls and the ammonia is allowed to escape. The valve is shut again and steam admitted a second time for 20 minutes. The reaction proceeds at 200-lb. pressure for 1½ hours. The escaping gas contains 25 p.c. ammonia and 75 p.c. steam. It passes through a header and 7 mud drums followed by 7 ammonia column stills, each 10 feet diameter and 25 feet high, containing 16 horizontal plates. The gas enters at the bottom and bubbles through caps over 4-inch holes in the plates, passing to 14 condensers arranged in 7 sets of 2 in series, containing vertical tubes through which water circulates, where steam is condensed. The ammonia gas passes through a 28-inch pipe, tapped by two 20-inch mains, one conveying 55 p.c. of the ammonia to two 60,000 cubic feet gasholders for the ammonia oxidation plant, and the other 45 p.c. to the neutralisation plant for ammonium nitrate. The capacity of the plant is 1000 tons of ammonia gas per week.

The autoclave sludge is blown out through an 8-inch outlet at the bottom by means of steam or air and falls by gravity to 20 rotary filters, 5 spare, operating under 20-inch mercury suction, where the 2 p.c. caustic soda solution is drawn off and returned to the autoclaves.

The absorption of nitrogen by carbide is reversible at 1360°; the best temperature for the reaction is 1000°–1100°. On account of the reversibility of the reaction at very high temperatures the molten carbide from the carbide furnaces cannot be used directly, but must first be cooled and powdered.

Polzenius (D. R. P. 163320, 1901) found that the addition of calcium chloride to the carbide lowered the temperature at which nitrogen is absorbed to 700°–800°, so that the reaction could be carried out in retorts externally heated by fuel. This process was adopted by the A. G. für Stickstoffdünger at Westeregeln and at Knapsack, near Cologne. The latter works has a capacity of 11,000 tons of cyanamide per month. There are 10 carbide furnaces of the usual open rectangular type (*see* above), charged by hand with a mixture of 100 parts of quicklime and 66 of anthracite. The main portion of the carbide is reduced to nut-size and is then mixed with 10 per cent. of calcium chloride in tube mills, containing steel rods.

The mixture is fed to the cyanamide cans, which are rectangular, 18 inches by 12 inches by 9 inches, of thin sheet iron with a perforated bottom which can be removed in emptying. The bottom and sides are lined with paper before filling, and a piece of cardboard is laid on top of the charge. Fifteen cans are loaded on a car, which runs on a track the whole length of the furnaces.

There are 16 furnaces, about 120 feet long and 6 feet diameter, of 2-inch iron plates, set in firebrick and heated by lignite gas. Nitrogen, from a Linde apparatus of 1800 cu. m. per hour capacity, is fed in at the cooler end of the furnaces, and the carbide trucks run in at the opposite end. Every 8 hours 3 cars are pushed into the furnace by an electric ram. At the end of 24 hours, 3 cars, or 45 cans, of cyanamide have reached the nitrogen end of the furnace, are pushed out, and allowed to cool. The product is then ground in the same manner as the carbide. It contains 16–22 p.c. N and 0·75 p.c. CaC_2 (*cf.* Allmand and Williams, J. Soc. Chem. Ind 1919, 38, 304 R). A similar process is in use in the Rumanian factory at Söras (Chim et Ind., Jan., 1922).

A continuous method was described by Tofani (D. R. P. 246077, 1910), but the most successful method appears to be that of Carlson, used by the Ljunga Verk, Stockholms Superfosfat Fabriks Aktiebolag, Stockholm (Eng. Pat. 123796, 1919). In this process, shaft-furnaces with shelves are used, and the mixture of carbide, with an indifferent substance such as lime, and calcium chloride or fluoride, is moved from shelf to shelf down the furnace. There are 8–10 shelves per furnace, with automatic rakes for moving the carbide. The absorption of nitrogen is 80 p.c. In the Tofani furnace the powder dropped directly down the furnace, and the contact with the gas was much less complete. The product obtained in the Carlson furnace is in the form of coke-like lumps a few inches in diameter, instead of a hard solid cake, as in previous processes. It is taken out by opening a hole at the bottom, constructed as a double lock. The heating is effected by an electric arc in each furnace, the consumption of electrodes being 3–5 kg. per metric ton of cyanamide. The output of each furnace is 20–25 tons cyanamide per 24 hours. About 15 kw. hr., measured at the furnace, are used per kg. nitrogen fixed in the form of cyanamide, as compared with 20 kw. hr. in discontinuous processes, and the product contains about 20 p.c. of combined nitrogen. The advantages claimed for the process are: reduction in carbide consumption to 720–730 kg. carbide of 300 litres per ton cyanamide; a saving of 10 p.c. on erection costs; a product richer in combined nitrogen; and lower working costs consequent on the use of a continuous process. Although the method is at present used only in the Stockholm works, which produce 20,000 tons cyanamide annually, it is regarded as very promising, and may be considerably extended.

Uses of Nitrolim. Crude calcium cyanamide is known as *nitrolim*, and, after treatment, is largely used as a fertiliser. Under British conditions (J. Soc. Chem. Ind. 1917, 256; 1918, 146 R) it appears that the fertilising value of nitrolim nitrogen is about 94 p.c. that of ammonia nitrogen. Experiments made in Egypt show that nitrolim does not undergo sufficiently rapid nitrification in the soil to satisfy the needs of some of the rapidly growing crops; calcium nitrate is then preferable (*see also* Pranke, Cyanamid, Easton, Pa., 1913).

The mode of decomposition of nitrolim in the soil is not simple (*see* Cowie, J. Agric. Sci. 1919, 113; Mazé, Vila, and Lemoigne, Compt. rend. 1919, 169, 804, 921; Hall, Fertilisers and Manures, 1919). On exposure to moist air, small quantities of ammonia are liberated:

$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

but free cyanamide is also formed:

$$CaCN_2+CO_2+H_2O=CaCO_3+CN{\cdot}NH_2.$$

The latter substance may then combine with water to form urea: $CN{\cdot}NH_2+H_2O=CO(NH_2)_2$. Urea is converted by fermentation into ammonium carbonate:

$$CO(NH_2)_2+2H_2O=(NH_4)_2CO_3.$$

The latter is readily oxidised to nitrates in the soil. Other substances may be formed, such as basic calcium cyanamide, and dicyandiamide $(CN{\cdot}NH_2)_2$; the latter compound has been said to be prejudicial to crop growth (*see* Pranke, *l.c.*). In order to minimise the corrosive and dusty character of nitrolim, the free lime is hydrated by water and the dry hydrated material is then treated with mineral or tar oil. In this way its nitrogen content is reduced to about 16 p.c. Numerous colloidal and other materials have also been proposed for the treatment of nitrolim, but hydration and oiling appear to be satisfactory. In this process there is an increase in weight of about 10 p.c. of the cyanamide (*see* Worden, Technology of Cellulose Esters, Vol. I., ii, 929).

Cyanides from Nitrolim. When crude nitrolim is fused with common salt or with sodium carbonate, 90–95 p.c. of the nitrogen is converted into sodium cyanide:

$$CaCN_2+C+2NaCl=CaCl_2+2NaCN$$
$$CaCN_2+C+Na_2CO_3=CaCO_3+2NaCN$$

The product, when salt is used, contains about 30 p.c. of NaCN, and can be used directly for the extraction of gold. Pure NaCN is prepared from it by liberating HCN by dilute acid and absorbing the gas in caustic soda. Metallic sodium has also been used in the preparation of cyanides, but no details of any process have been disclosed. The chief objection to all processes involving aqueous extraction of cyanides from melts, and subsequent evaporation, is the loss which occurs during the latter process, and the inferior product obtained as compared with that produced by the fusion process.

Landis (Chem. and Met. Eng. 1920, 22, 265) prepares cyanides by fusing crude cyanamide ($CaCN_2+C$) in an electric furnace, either alone or mixed with common salt. A plant was installed at Niagara late in 1916 consisting of 7 furnaces. The addition of a little carbide prevents foaming on adding cyanamide to the fused common salt. Contrary to previous specifications, the temperature should be as high as possible. In the latest type of furnace, single-phase current is used, with a conducting hearth and one suspended electrode. The production is 30 tons per day of a product containing the equivalent of 36·5 p.c. NaCN. The reaction is $CaCN_2+C=Ca(CN)_2$, and a mixture of 2 parts of cyanamide with rather less than 1 part of common salt is used. The product is a mixture of calcium cyanide, sodium chloride, free lime, with less than 1 p.c. calcium carbide, cyanamide, and ash impurities. The use of cyanamide without salt has been made the subject of experiments.

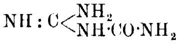
Anhydrous hydrocyanic acid is made in 2 factories in California and is sent out in the liquid state for fumigating purposes, especially in destroying spiders in the orange groves of Florida.

Other Products from Nitrolim. Dicyanodiamide (Zeitsch. angew. Chem. 1903, 520) is prepared by the action of cold water on calcium cyanamide:

$$2CaCN_2+4H_2O=2Ca(OH)_2+(CN{\cdot}NH_2)_2.$$

It is used in the manufacture of dyes, and in reducing the temperature of explosion when mixed with explosives such as cordite, which alone rapidly destroy the rifling of guns. The American Cyanamid Co. prepare a fertiliser known as 'Amophos,' consisting chiefly of ammonium phosphate, from cyanamide ammonia. Nitrolim may also be mixed with basic slag, superphosphate, and potash salts for fertilising purposes.

When calcium cyanamide is treated with acids or alkalies, dicyanodiamidine,



$$NH:C\begin{matrix}\diagup NH_2\\ \diagdown NH{\cdot}CO{\cdot}NH_2\end{matrix}$$

is formed, from which urea and guanidine may be obtained. Guanidine is prepared by heating with acids in an autoclave. Guanidine nitrate and nitroguanidine are used as deterrents (*see* dicyanodiamine) in explosives. Urea may be obtained directly from calcium cyanamide by heating with 10–20 p.c. sulphuric acid at 20°–25°, and is proposed as an effective fertiliser. Veronal and creatin are also produced from cyanamide, and lead and copper cyanamides are said to be of technical importance (*see* Carlson, Zeitsch. angew. Chem. 1914, 27, iii, 724; Pranke, Cyanamid, Easton, Pa. 1913). 'Ferrodur' is a material containing calcium cyanamide used in case hardening.

For analysis of cyanamide, *see* Brioux, Ann. Chim. anal. 1910, 15, 341; Caro, Zeitsch. angew. Chem. 1910, 23, 2405; Perotti, Gazz. chim. ital. 1905, 35, ii, 228; Kappen, Chem. Zeit. 1911, 35, 950; Monnier, *ibid.* 601; Stutzer, *ibid.* 694; Grube and Krüger, Zeitsch. angew. Chem. 1914, 27, 326; Morell and Burgen, J. C. S. 1914, 105, 576; Stutzer and Söll, Zeitsch. angew. Chem. 1910, 23, 1873; Kirchoff, Chem. Zeit. 1912, 36, 1058; Weston and Ellis, 7th Int. Congress Rep., Sect. 1., p. 69; N. Kameyama, J. Coll. Eng. Tokyo, 1920, 10, 173.

The Arc Process. The pioneering work on which the modern industrial method of nitrogen fixation by the union of oxygen and nitrogen in the electric arc is based was carried out almost entirely by English scientists. Cavendish in 1784 observed the formation of nitric acid when electric sparks were passed through air over water and when oxygen containing nitrogen is exploded with hydrogen. No acid is formed in the explosion of hydrogen and air, since the flame temperature is then not high enough to bring about the union of oxygen and nitrogen, the reaction being endothermic. The really classical research, on which all modern processes are based, is that of Lord Rayleigh in 1897 (J. C. S. 1897, 71, 181). In his memorable experiment, which resulted in the separation of argon from atmospheric nitrogen, Lord Rayleigh used a glass globe of 50 litres capacity, containing a mixture of 9 vols. of air and 11 vols. of oxygen, in which an electric flame was burning. The resulting oxides of nitrogen were absorbed by allowing a fountain of caustic soda solution to play over the inside of the globe. This also served to keep the vessel cool. An absorption of 21 litres of gas per hour was obtained with 0·8 kw., which gives a production of 46 grm. of nitric acid per kw. hr. In the most efficient modern arc furnaces the yield is 62 grm. HNO_3 per kw. hr. Lord Rayleigh was the first to point the way to the possibility of utilising the nitrogen of the atmosphere in an economical manner.

Attempts were made to apply the results of Rayleigh to the industrial fixation of nitrogen. The first was that of Bradley and Lovejoy at Niagara, in 1902, although small scale experiments were carried out in Manchester in 1900 by Macdougall and Howles (*see* Thompson, Applied Electrochemistry, 1911, p. 276). None of the earlier attempts was successful, and the first real step in the direction of a technical process was made by Birkeland of Christiania in conjunction with Eyde, the engineer. The results of their work was the establishment in 1903, by the Scandinavian French Company, of a factory at Notodden, in Norway, known as the Norsk Hydroelektrisk Kvaelstofaktieselskab (the Norwegian Hydro-electric Fertiliser Company). In 1906 the Norwegian company joined forces with the German firms, the Farbenfabrik vormals F. Bayer and Co., Elberfeld, the Aktiengesellschaft für Anilinfabrikation of Berlin, and the Badische Anilin und Soda Fabrik (which really controlled the other two firms). In later developments the German interests were eliminated, and the whole undertaking is now owned by the Société Norvegienne de l'Azote.

The establishment of the arc process in Norway was possible on account of the abundance of cheap water power which could be harnessed to hydro-electric undertakings. The potential and developed hydro-electric power of the world has been stated as follows:—

	Potential h.p.	Developed h.p.
United States .	20,000,000	5,000,000
Canada . .	6,000,000	1,756,791
France . .	6,000,000	500,000
Norway . .	5,500,000	850,000
Spain . .	5,000,000	300,000
Italy . .	5,000,000	750,000
Sweden . .	5,000,000	600,000
Switzerland .	1,500,000	400,000
Germany .	1,000,000	500,000
Great Britain . .	700,000	60,000

The power for the Notodden works is derived from the Svaelgfoss, about 1½ miles up the valley, and the water falling over the Rjukanfoss generates in its passage to the Hitterdal lake 40,000 h.p. at the Svaelgfoss, 15,000 h.p. at the Lienfoss, and 20,000 h.p. at the Tinfoss, making a total of 75,000 h.p. at Notodden.

The two new works at Rjukan have recently been put into operation, and about 380,000 h.p. are now expended in Norway on the arc process.

The Rjukan works alone use 300,000 h.p., and are said to have cost £3,000,000. This works out at about £26 per ton of nitric acid per annum. The cost of plant, including the reservoirs and turbines, is high in the case of the arc process, but as no materials except water and air are used, with limestone if calcium nitrate is made, the products can be cheaply manufactured if abundant sources of water-power are available. The possibility of operating the arc process with coal-fired power plant has been considered (Nitrogen Products Committee Report, 1920); the conclusion reached was that, as the process has been successfully operated intermittently in Italy on off-peak electric power, it might be possible in this country to use it as an outlet for large blocks of off-peak power from large central coal-fired electric generating stations, thus enabling the generators to work at a high load factor, and reducing working expenses. The unexpected movement of coal prices has somewhat altered the situation.

The power used by the Norwegian works is derived from the Rjukan fall, the water of which is collected in the Moesvand Lake, which has a capacity of 768,000,000 cu. m. This reservoir, which is closed by a large dam, feeds the river Maana, the water of which is conducted through a tunnel 4 km. long and 26 sq. m. in section to a collecting house, from which it passes through ten steel flumes or conduits, 2 m. in diameter, which carry 50 cu m of water per second to the power house. The Rjukanfoss power house, which is 110 m. long and 20 m. broad, contains ten turbines, each of 14,500 h.p., directly coupled to the generators (Fig. 1). The electric current is transmitted through sixty cables, some of copper and some of aluminium, to the Rjukan I works at Vermork, and to the Rjukan II works at Saaheim, both approximately the same size, in which the total of 300,000 h.p. is applied.

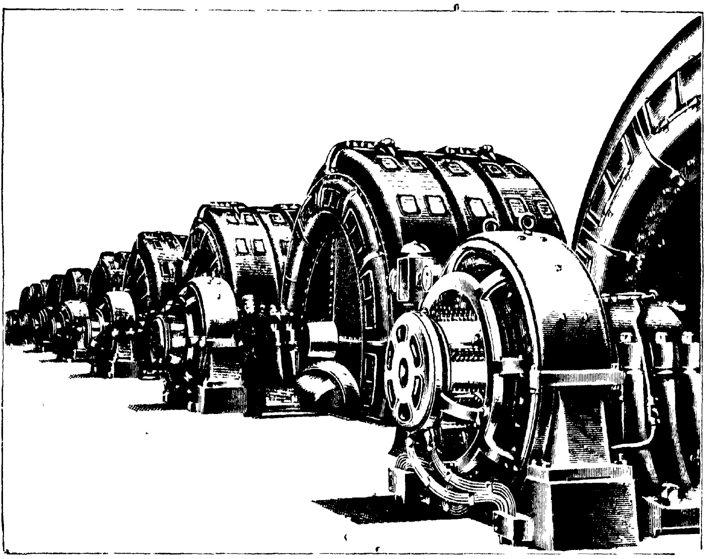


FIG. 1.

Rjukanfoss Power House.

In Rjukan I there are two types of furnaces, the Birkeland and Eyde, and the Schonherr. At Rjukan II Birkeland and Eyde furnaces alone are used. Another factory of the Norwegian company is situated at Pierrefitte, on the French side of the Pyrenees, where water power from two lakes is used. There is a similar factory on the Spanish side, but this is not yet in operation. The works at Pierrefitte uses 8000 kw., producing 4000 tons of nitric acid per annum. The water is obtained from the lake at Cauterets, at an altitude of 280 m., and that at Luz St. Sauveur, at an altitude of 140 m. It is conducted through six flumes running down the Pic de Soulom, three to each lake, 3 and 4 feet diameter, respectively. The high-pressure water passes to Pelton wheels, and the low-pressure to turbines, in each case coupled directly to alternators. These supply in addition the power for the electrified portion of the Midi Railway from Lourdes to Cauterets. The current is transformed to 10,000 volts for transmission to the works. There are four of the newest type of Birkeland-Eyde furnaces, about 10 feet diameter, operating on single phase at 6000 volts, and using up to 4000 kw. each. About 5000 cu. m. of air is drawn through each furnace per hour.

The power used for nitrogen fixation is shown in the table below, taken from the Statistical Supplement to the N. P. C. Report. This table shows only the two main processes in which power is a primary factor. The installed capacity of the power plants employed for nitrogen fixation in 1920 amounted to over a million kilowatts when allowance is made for the reserves always provided. The actual number of kilowatt hours required to produce the full output of the arc and cyanamide plants in 1920 was nearly double the combined actual output of the whole of the electricity stations of the British Isles, including lighting, power, and traction.

WORLD'S CONSUMPTION OF POWER IN NITROGEN FIXATION.

Process	1913		1920	
	Installed capacity tons nitrogen per annum	Actual power required in continuous kw	Installed capacity, in tons nitrogen per annum	Actual power required in continuous kw.
Cyanamide	59,500	130,000	325,500	715,000
Arc .	16,900	142,000	38,300	316,000

These figures give for the power requirements: arc process, 8·35-8·4 kw. yr., and for the cyanamide process, 2·2 kw. yr., per ton of nitrogen fixed.

Theoretical Considerations. For the equilibrium constant of the reaction $N_2+O_2 \rightleftarrows 2NO$ Nernst (Zeitsch. anorg. Chem. 1906, 49, 213; Gottinger Nachrichten, 1904, 261) gives an expression which may be simplified to

$$\log \sqrt{K} = 0{\cdot}5441 - 4725{\cdot}5/T$$

where T is the absolute temperature C., and

$$K = C^2_{NO}/C_{N_2} \times C_{O_2}$$

In the case of air as the initial mixture of N_2 and O_2, when x p c. of NO by volume has been formed in equilibrium, $K = x^2/(79{\cdot}2-\frac{1}{2}x)(20{\cdot}8-\frac{1}{2}x)$, and, therefore, since x is small,

$$x = 40{\cdot}8\sqrt{K}/(1+0{\cdot}62\sqrt{K})$$

very approximately. From these equations the values of x=p.c. NO in Table I. have been calculated. They agree fairly well with the observed numbers, which were obtained by exploding a mixture of electrolytic gas and air, and by drawing air through platinum and iridium tubes heated electrically. The reaction absorbs heat: $N_2+O_2=2NO-2\times21{\cdot}6$ kg. cal.

TABLE I.—EQUILIBRIUM YIELDS OF NO IN AIR.

Temperature °C. absolute	P.c. NO by volume obsd.	P.c. NO by volume calcd.
1811 . .	0·37	0·35
1877 . .	0 42	0·43
2033 . .	0·64	0·67
2195 . .	0·97	0·98
2580 . .	2·05	2·02
2675 . .	2·23	2·35
3200 . .	5·0 about	4·39

The same values of K apply, of course, to any initial mixture of nitrogen and oxygen as well as air, but the relation between x and K is different for each mixture. For the important case of equal volumes of oxygen and nitrogen we have $K=x^2/(50-\frac{1}{2}x)(50-\frac{1}{2}x)$, or, very approximately, since x is small,

$$x = 50\sqrt{K}/(1+0{\cdot}5\sqrt{K}).$$

The increased yield with the mixture N_2+O_2 as compared with air is, therefore, approximately 18 p.c. Higher yields claimed (*see* Nitrum process) must, therefore, depend on other circumstances, such as more rapid cooling. Oxygen has a thermal conductivity 7 p.c. greater than that of nitrogen. Haber and Koenig (Zeitsch. Elektrochem. 1907, 13, 725) obtained 14·5 p.c. of NO from N_2+O_2. By using a short arc in a water-cooled tube these experimenters (*ibid.* 1908, 14, 689) obtained 17·8 p.c. NO. The same final concentration was obtained with N_2+O_2 and NO as initial gas, indicating equilibrium. Increase of pressure does not increase the yield. Similar experiments were made by Holwech (*ibid.* 1910, 16, 369), Haber and Holwech (*ibid.* 810), Holwech and Koenig (*ibid.* 803—cooled arcs), Haber, Koenig, and Platou (*ibid.* 786, 796). The yields for a given expenditure of energy are much larger than those found in other experiments, such as those of Nernst; in the most favourable cases they amount to 80 grm. HNO_3 per kw. hr. The percentage of NO in the resulting gases also corresponds, on the thermodynamic theory, with impossibly high temperatures (the temperature 3200 corresponds with only about 5 p.c. of NO, as is seen from Table I.). Haber considers that a cool arc is more favourable to NO formation than exposure to very high temperatures followed by rapid cooling, and that electronic impacts play a part under certain conditions (*see* Jellinek, Gasreaktione, 1913, p. 780).

The velocities of formation and decomposition of nitric oxide have been determined. Below 3000° the reaction is bimolecular:

$$N_2+O_2 \rightleftarrows 2NO$$

above 3000° it is said to be unimolecular (Le Blanc and Nuranen, Zeitsch. Elektrochem. 1907, 13, 303). In the bimolecular case, the velocity equation is:—

$$dx/dt = k_1(C_O-\tfrac{1}{2}x)(C_N-\tfrac{1}{2}x) - k_2x^2$$

where C_N and C_O are the initial concentrations of N_2 and O_2 in percentages by volume, and x the percentage of NO present at a given instant. The velocity constants k_1 and k_2, representing the rate of formation and decomposition of NO respectively for unit concentrations, have been determined experimentally by Jellinek (Zeitsch. Elektrochem. 1907, 13, 303; Zeitsch. anorg. Chem. 1906, 49, 229), whose results are given in Table II. The time for half decomposition of pure NO into N_2 and O_2 is very approximately $t_2=1/k_2$; the time for half the possible nitrification of air, *i.e.* half the theoretically possible production of NO, is approximately $t_1=1{\cdot}36/\sqrt{k_1k_2}$. The velocity constants depend very much on the temperature; Steinmetz (Chem. & Met. Eng. 1920, 22, 299) calculates from Jellinek's results $\log k_2=\overline{11}{\cdot}113+5{\cdot}731\times10^{-3}T$, when t is in seconds. From this, and the relation $k_1=k_2K$, the values given in Tables II. and III. have been calculated. The values of K have been obtained from the formula:

$$\log K = 1{\cdot}048 - 9380/T$$

given by Steinmetz, which is in good agreement with the formula of Nernst previously quoted.

TABLE II.—VELOCITIES OF DECOMPOSITION OF NO.

Time in minutes for 50 p.c. decomposition of pure NO at atm. press. into N_2 and O_2.

Abs. temp. °C.	Time in mins. obsd.	$60t_2$ mins calcd. $=1/k_2$	k_2 for second as unit of time
900	$7\cdot35\times10^{3}$	$8\cdot9\times10^{8}$	$1\cdot87\times10^{-6}$
1100	$5\cdot80\times10^{2}$	$6\cdot4\times10^{2}$	$2\cdot61\times10^{-5}$
1300	$4\cdot43\times10$	$4\cdot5\times10$	$3\cdot66\times10^{-4}$
1500	$3\cdot30$	$2\cdot35$	$5\cdot12\times10^{-3}$
1700	$2\cdot47\times10^{-1}$	$2\cdot33\times10^{-1}$	$7\cdot17\times10^{-2}$
1900	$1\cdot74\times10^{-2}$	$1\cdot56\times10^{-2}$	$1\cdot002$
2100	$1\cdot21\times10^{-3}$	$1\cdot18\times10^{-3}$	$1\cdot41\times10$
2300	$8\cdot40\times10^{-5}$	$8\cdot45\times10^{-5}$	$1\cdot97\times10^{2}$
2500	$5\cdot76\times10^{-6}$	$6\cdot06\times10^{-6}$	$2\cdot75\times10^{3}$
2700	$3\cdot92\times10^{-7}$	$4\cdot43\times10^{-7}$	$3\cdot85\times10^{4}$
2900	$3\cdot35\times10^{-8}$	$3\cdot08\times10^{-8}$	$5\cdot40\times10^{5}$
3100	$2\cdot25\times10^{-9}$	$2\cdot20\times10^{-9}$	$7\cdot57\times10^{6}$
3500	—	$1\cdot13\times10^{-11}$	$1\cdot48\times10^{9}$
4100	—	$4\cdot10\times10^{-15}$	$4\cdot07\times10^{12}$

TABLE III.—VELOCITY OF FORMATION OF NO FROM AIR.

Time in minutes for production of half the theoretically possible amount of NO.

Abs. temp. °C.	Time in mins. obsd.	$60t_1$ $=1\cdot36/\sqrt{k_1k_2}$ mins calcd.	k_1 for second as unit of time
900	—	—	$7\cdot89\times10^{-16}$
1500	$1\cdot81\times10^{3}$	$1\cdot77\times10^{3}$	$3\cdot19\times10^{-8}$
1700	$5\cdot90\times10$	$5\cdot45\times10$	$2\cdot43\times10^{-6}$
1900	$2\cdot08$	$1\cdot99$	$1\cdot29\times10^{-4}$
2100	$8\cdot43\times10^{-2}$	$8\cdot22\times10^{-2}$	$5\cdot36\times10^{-3}$
2300	$3\cdot75\times10^{-3}$	$3\cdot76\times10^{-3}$	$1\cdot84\times10^{-1}$
2500	$1\cdot77\times10^{-4}$	$1\cdot85\times10^{-4}$	$5\cdot44$
2700	$8\cdot75\times10^{-6}$	$9\cdot60\times10^{-6}$	$1\cdot44\times10^{2}$
2900	$5\cdot75\times10^{-7}$	$5\cdot20\times10^{-7}$	$3\cdot52\times10^{3}$
3100	$3\cdot10\times10^{-8}$	$2\cdot87\times10^{-8}$	$7\cdot96\times10^{4}$
3500	—	10^{-10}	$3\cdot46\times10^{7}$
4100	—	$2\cdot3\times10^{-14}$	$2\cdot34\times10^{11}$

From these results it follows that, if the combination in the arc occurs purely on account of the absorption of heat, the best results should be obtained when the air is heated to a temperature not less than 3000°, and then cooled with all possible speed below the temperature, say 1000°, at which the velocity of decomposition of the nitric oxide formed at the higher temperature has become inappreciable. This conclusion is confirmed by experiment. Since the rapidity of cooling attainable practically limits the amount of nitric oxide remaining, there will be no point in going above a certain temperature in the arc, at which the equilibrium concentration of NO is not less than the residual concentration possible under the most favourable conditions of cooling with the given apparatus.

In the commercial operation of the arc process, a concentration of 2 p.c. of NO by volume is attained as a maximum from air and usually only a little over 1 p.c. The temperature corresponding to 2 p.c. is, according to the above results, about 2500°. It is thus possible to calculate the minimum expenditure of energy necessary in the furnace, assuming this to be the mean temperature of the gases. This energy is the electrical equivalent of the heat absorbed in the reaction $N_2+O_2=2NO$, plus that required to raise the temperature of the gases to 2500°. Since the mean specific heats of the three gases at constant pressure are approximately equal, and given by the expression $6\cdot8+0\cdot0006t$ grm. cal. per grm. mol., we have, as the absorption of energy for heating, 14 grms N_2 and 16 grms. O_2 to 2500°:—

$$\tfrac{1}{2}(6\cdot8+2500\times0\cdot0006)=20,600 \text{ grm. cal.}$$

If we add to this the energy 21,600 grm. cal. for the production of 30 grms. NO (100 p.c. conversion), we find as the *minimum* energy required 20,600+21,600=42,200 grm. cal., or about 0·05 kw. hr. But in practice it is found necessary to expend 1 kw. hr. (2 p.c. conversion) in the formation of 30 grms., or 1 grm. molecule, of nitric oxide, hence the energy efficiency of the arc process is 0·05×100=5 p.c. A certain amount of this energy is recoverable in the less available form of heat from the hot gases, by passing the latter through boiler tubes. The *maximum* amount so recoverable is about 5 p.c. of the initial energy after all requirements for evaporation and cooling have been met. The latter utilise about 8 p.c. The arc process as operated is clearly very wasteful of energy, only about 10 p.c. of the latter being usefully applied in the maximum. It can, therefore, be used economically only when a very cheap source of energy is available. This is provided by large water-power sources, or, in Germany, by the utilisation of brown coal (or lignite) from which electrical energy is produced at a cost of about 0·4*d*. (2·8 pfg.) per kw. hr., as compared with at least 1·5*d*. per kw. hr. from British coal under present conditions. The cheap coal supplies of Natal, where coal is obtainable at a cost of about 3*s*. per ton, and the large undeveloped water powers of Egypt (Assuan Dam) and Newfoundland, offer prospects of utilisation by the arc process in these countries.

The Birkeland and Eyde Process. In this type of furnace the arc between the electrodes is maintained by an alternating current and is spread by a strong magnetic field at right angles to the axis of the electrodes. The current filament tends to move at right angles to its length in the magnetic field, and is blown into a half disc at each half period of the current. The filament breaks when the resistance along it is greater than that of a new arc in the cooler air between the points of the electrodes (Trans. Faraday Soc. 1906, 2, 98). The half discs succeed each other with great rapidity on each side of the electrode axis, and the impression on the eye is that of a steady circular sheet of flame (*see* Andriessens, Zeitsch. Elektrochem. 1919, 25, 255).

The electric flame is produced in a flat box of refractory material (Eyde, J. Roy. Soc. Arts, 1909, 57, 568), the walls of which do not in actual working become heated beyond 1000°. A recent type of furnace is shown in section in Fig. 2. The electrodes are U-shaped copper tubes, 1 inch wide, separated by a distance of one-eighth inch to form a gap for the initiation of the arc. The position of the electrodes is regulated by screws outside the furnace. One electrode is earthed. The applied voltage is 6500. In the most recent type of furnace the air is aspirated into the furnace through grids of iron netting placed opposite the inlet ports; in the older types the air is forced through by Roots blowers. The air is divided by channels in the fireclay lining of the furnace, so as to be directed uniformly on both sides of the arc flame. During the brief contact of the air with the intensely hot flame, combination of oxygen and nitrogen takes place. The gases are then swept out of the furnace and cooled with great rapidity to about 1000°, below which temperature nitric oxide is stable.

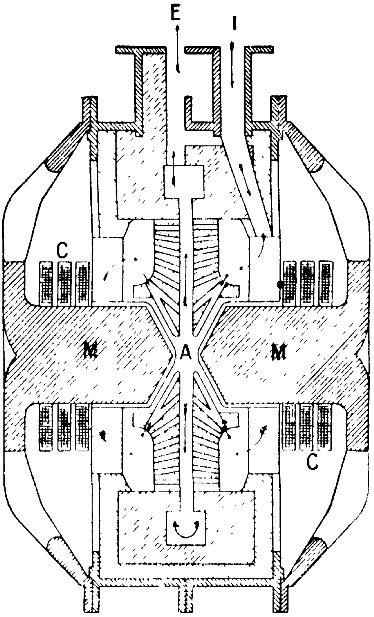


Fig. 2.

New type of furnace showing the passage of the gases.

The electrodes are cooled by a rapid current of water passing through them. The latest types of Birkeland and Eyde furnaces are made in units taking 2000, 3000, or 4000 kw. The most economical size is said to be 3000 kw. The electrodes last 3–4 weeks, and are easily replaced in about 15 minutes when required. The temperature of the flame is estimated at 3000°–3500°; that of the escaping gases, of which about 74 cubic feet pass through the furnace per kw. hr., is about 1000°.

At Notodden there are 36 furnaces of the early type using 800 kw., working at 5000 volts. At Rjukan I there are about 120 furnaces, 40 Birkeland-Eyde and 80 Schönherr (see below); there are about the same number at Rjukan II, but there all the furnaces are of the Birkeland-Eyde type (Fig. 3). The concentration of nitric oxide in the gases immediately after leaving the furnace is about 1·25 p.c. by volume on the average. The gases are further cooled, and the oxides of nitrogen absorbed as nitric acid and as sodium nitrate and nitrite, in apparatus to be described later. About 97 p.c. of the fixed nitrogen is absorbed, 85 p.c. of this as 30 p.c. nitric acid and 15 p.c. as nitrite. The energy consumption in the Birkeland-Eyde process is estimated by the Nitrogen Products Committee as 1 kw. hour per 61 grms. of nitric acid, HNO_3, for overall

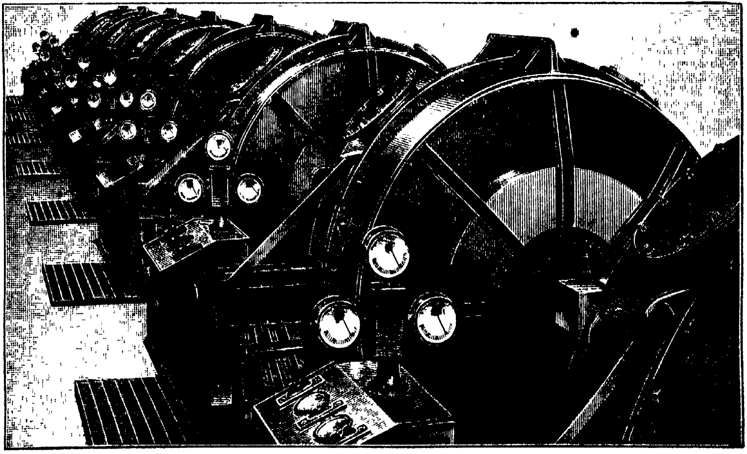


Fig. 3.

Birkeland-Eyde Furnaces at Rjukan.

working. The arc process has the advantage over other fixation methods in being direct and comparatively simple, and in the absence of objectionable by-products (*cf. Cyanamide*). Its disadvantages are the very expensive plant, including large power installations, and its dependence on cheap power. In localities where cheap water-power is available (*e.g.* £1·2 per kw. year in Norway) the latter factor has no weight.

The arc factory at Soulom, Pyrenees, embodies the latest improvements of the Birkeland-Eyde process. The current (see above) is supplied to the works by underground cables at 10,000 volts, a portion being stepped down at the works to 380 volts for lighting. The choking coils used in connection with the furnaces are water-cooled lead coils immersed in oil, having an iron core and an automatic thermometer operating at 50°–60°, at which temperature the current is cut off. The power loss in the choking coils is less than 1 p.c. Copper spirals, without iron cores, as used at Notodden, have been abandoned.

The furnace room contains four of the latest type of Birkeland-Eyde furnaces, about 10 feet diameter, operating on single phase up to 4,000 kw. Three are in use and one in reserve. The phases are interchangeable, one electrode being earthed. The furnaces are of brick, with a lining of special refractory stone of Norwegian origin, the whole enclosed in an iron casing. There is a lenticular cavity containing the electrodes, one wall of which is perforated by canals in communication with five equally-spaced suction intakes for air. After passing through the furnace, the air leaves at the bottom through a curved oval pipe about 2 feet in longest and 1 foot in shortest diameter, lined with resisting brick. This connects with the main flue, about 5 feet diameter, lined with resisting brick 18 inches thick, carrying away the gases, at about 1000°C., to the cooling and absorption plant. The gas is analysed at regular intervals by taking a sample from the main near the furnace in an exhausted globe.

The volume of air aspirated through each furnace is about 5,000 cu. m. per hour, and the percentage of NO in the furnace gas varies from 1·5 to 2 p.c. by volume. The air, as stated, is drawn through the whole system by two fans in series after the last absorption tower, each of 100 h.p. The drop in pressure through the furnace is about 1½ inches of water.

The electrodes are U-shaped copper tubes about 1 inch diameter, separated by about one-eighth inch and cooled by water circulating through the tubes. The position of the electrodes is adjusted by screws outside the furnace. The arc is deflected by a large electro-magnet placed in a cavity on that side of the furnace into which air is drawn. The air passes through channels in the magnet, and serves to keep the latter cool. Current for these magnets is obtained from the high-tension A.C. by a rotary converter. The average life of an electrode is from 3 to 4 weeks. The furnaces emit a deep roaring note, which, however, is not unpleasant.

The gas in the main leading from the furnace enters at about 900°C. into two Babcock boilers, each having about 300 sq. m. of heating surface and provided with superheaters and economisers. A considerable amount of steam is blown to waste after all requirements in the works for evaporation, concentration, &c., have been satisfied. After passing through the boiler firebox the gases leave at about 250° to the coolers. These are placed in the open air, and consist of four batteries of iron tubes, through which the gases pass, cooled in vertical tanks through which water flows.

The gas leaves the coolers for the oxidation tower, of sheet iron and of sufficient capacity to give one-minute contact to the gas before this enters the water towers. This is necessary to enable the nitric oxide to be partly converted into nitrogen peroxide before the gases come in contact with water. The gases leave the tower at 50°; the drop in pressure in the coolers is about 40 mm. of water; that in the oxidation tower 5 mm.

The gas now enters the absorption towers (Fig. 4). There are four of these, constructed of slabs of Norwegian granite clamped by 61 iron bands. The nature of the stone used for these towers is extremely important; Norwegian granite is practically the only material which has been found satisfactory, since other varieties tend to disintegrate in use in contact with the acid. The towers are 10-sided, 26·925 m. high inside and 7·3 m. uniform external diameter. The thickness varies from 350 mm. at the bottom, in steps of 300, 250 and 200 mm. to the top. The towers are mounted on concrete piers with all joints visible and accessible in case of leakage. The towers are packed with pieces of Norwegian quartz about the size of walnuts, the character of the packing being again of great importance. The towers are completely packed, with practically no free space. The gas enters at the bottom of the first tower and alternately at the top and bottom of successive towers. Acid is circulated in each tower by one montejus of iron-clad acid-resisting stoneware, having a capacity of 400 litres. The delivery is intermittent, the montejus emptying once every two or three minutes. There is one 4-inch stoneware pipe to each tower, with 'Almagam' rubber joints, for circulation in that tower, and a similar pipe for transferring acid from the next tower of the series. The circulation amounts to 10,000 litres of acid per hour. Circulation by centrifugal pumps would probably prove more effective. The top of the tower is domed, in sections joined with blue asbestos covered with tar.

The acid flows from each tower into a large granite tank with an aluminium cover, from which it is taken to the montejus. The strength of acid taken from the first tower, which is the strongest, is about 30 p.c. HNO_3. This can be raised to 52 p.c. by slower circulation, but the weaker acid gives the best all-round efficiency of absorption. The strengths in the succeeding towers are usually 20 p.c., 10 p.c., and 5 p.c., respectively. The time of passage of the gas through each tower is of the order of 1 minute.

After leaving the fourth acid tower, the gas enters an alkaline absorption tower, of sheet iron, about the same size as the acid towers, and also packed with quartz. Through this tower a solution of sodium carbonate, containing about 2 p.c. of caustic soda, is circulated. Sodium nitrate and nitrite are formed.

The drop in pressure through the tower system is as follows :—

First acid tower 125 mm. water.
Second acid tower 150 mm. water.
Third acid tower 100 mm. water.
Fourth acid tower 150 mm. water
Alkali tower 130 mm. water.

The time of passage of the gas through the alkali tower is also about 1 minute. The gas then passes through the fans to the open air. The exit, on very wet days, is distinctly red. On dry days the exit is said to be barely visible.

The overall absorption amounts to 96–97 p.c. of the oxidised nitrogen leaving the furnace. Of this 90 p.c. is recovered as nitric acid in the acid towers and 10 p.c. as sodium nitrate. These figures refer to the operation in which the mixture of sodium nitrate and nitrite obtained in the alkali tower is treated with dilute nitric acid to form sodium nitrate and the oxides of nitrogen evolved passed back to the acid towers for absorption. If the recovery is taken on the acid towers and alkali tower without subsequent treatment, it is stated that about 85 p.c. of the oxides absorbed are received in the acid towers and 15 p.c. in the alkali tower. The yield reckoned on acid and sodium nitrate, compared with power entering the factory and used for all purposes, was stated to be 550 kg. HNO_3 per kw. yr. If this is referred to power measured at the switchboard and used for furnace purposes only, the yield is 560 kg. HNO_3 per kw. yr., or about 63 gm. HNO_3 per kw. hr.

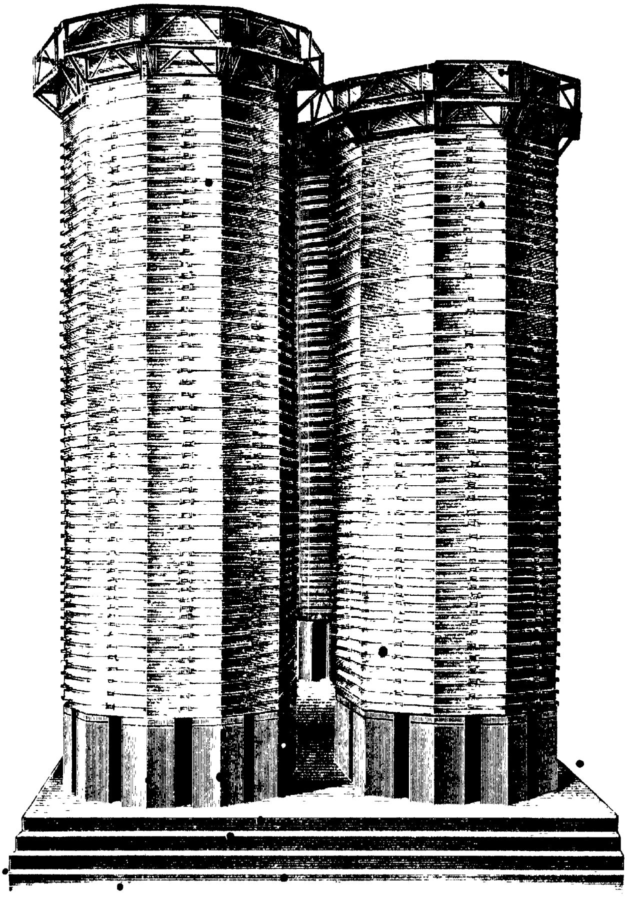


FIG. 4.

Absorption Towers.

The primary products of the absorption system are dilute nitric acid (30 p.c. HNO_3) and a solution of sodium nitrate, or if the solution from the alkali towers is not treated with acid, a solution of sodium nitrate and nitrite. The acid may be concentrated or converted into calcium nitrate. The sodium nitrate and nitrite are evaporated and sold for use in sulphuric acid chamber plants, or the nitrite is recovered in crystals for dye-making and other purposes.

Concentration of the Nitric Acid. The nitric acid is concentrated in a very efficient apparatus, due to Collet.

The 30 p.c. acid from the towers is pumped to a reservoir from which it descends to 4 granite towers, 10 feet diameter and 50 feet high, lined with acid-resisting stone and packed with quartz. In these it meets with steam from the weak acid concentrating plant, next described, and receives a preliminary concentration. The acid before entering the towers is also preheated by waste steam from another part of the plant. The concentration apparatus proper consists of steam-jacketed tubes. To each preliminary tower is attached a battery of four sets of four tantiron tubes, *i.e.* 16 tubes in all. Four tubes are arranged vertically around a bell-shaped head, and steam of 115 lbs. is passed through the jackets. Four of these evaporators form a unit attached to each of the four towers. Evaporation is effected at atmospheric pressure and the acid brought to 60 p.c. HNO_3. The 60 p.c. acid is collected in four granite reservoirs, and is pumped from these to a single large reservoir at the top of the building, from which it flows to two octagonal granite towers, 8 feet diameter and 30 feet high, one being in reserve. Into the same tower flows a stream of 80 p.c. sulphuric acid from a tank alongside the 60 p.c. nitric acid tank. Nitric acid of 96–97 p.c. strength is distilled over and is condensed in aluminium S-pipes placed between the two towers. The acid collected is sent down a small granite tower through which compressed air is passed to remove oxides of nitrogen, which pass to the absorption plant. The diluted sulphuric acid (60–65 p.c.) is concentrated in an apparatus similar to that used for making the 60 p.c. nitric acid, except that it works under vacuum, maintained by a vertical fall-pipe and water condensing jet. This apparatus for the concentration is very efficient, but is expensive. The strong acid is transported in strong earthenware bottles, holding 80 gals.

Sodium nitrate is prepared as previously described from the liquor obtained from the alkali tower, or by neutralising the tower acid with soda-ash, the oxides of nitrogen evolved being removed by fans. Sodium nitrite is concentrated in an apparatus similar to that used for nitric acid, the final concentration being carried out in 5 pans, 5 feet by 20 feet by 2 feet, heated by steam coils. Both salts are dried in hydro-extractors and bagged. About 2000–3000 tons of nitrite are made annually. Final drying of sodium nitrite may also be effected by Bühler's drying apparatus, Fig. 5. A is an air heater, B a pump, whereby air raised to a temperature of 100° is forced through the apparatus in the direction indicated by the arrows. The sodium nitrite enters at the entrance roller C and is forced through the drying tube into the cyclone D. The air is filtered in the air filter E and escapes through the outlet tube H. The passage of the sodium nitrite through the apparatus occupies 5–7 seconds, when it collects in the cyclone and is removed directly into casks by means of the outlet roller K.

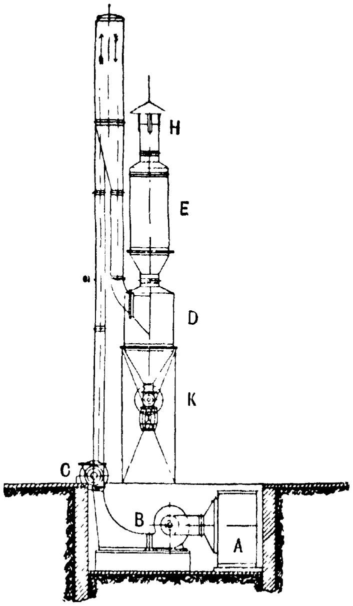


Fig. 5

Nitrate of lime. The nitric acid from the towers is run through a series of granite tanks filled with limestone, until the liquid contains not more than 0·5 p.c. of nitric acid, which is neutralised by the addition of lime. The liquid is then evaporated in vacuum pans until it has a sp.gr. 1·9, and run into iron drums holding 380 litres, when it sets to a hard mass and is thus exported for chemical purposes; or it is run on to shallow trays and when cold is broken up, ground to a coarse powder, and sent out as a manure in wooden casks. It varies in appearance from red-brown to black, according to the nature of the limestone from which it is made, and has the following composition—

N = 13·1 p.c., corresponding to 77·0 p.c. $Ca(NO_3)_2$
Water . . . . 21·5 ,,
Insoluble in water—
Fe_2O_3; Al_2O_3; humus . 1·5 ,,

Ammonium nitrate is prepared at Notodden and Rjukan by neutralising the 30 p.c. nitric acid with pure ammonia liquor (sp.gr. 0·880) formerly imported from England but now made from cyanamide. The resulting liquid is filtered, evaporated in vacuum pans until it has a sp.gr. 1·35, and is then allowed to crystallise. The crystals are centrifuged and dried in a Bühler's apparatus, when they contain 99·9 p.c. NH_4NO_3. In 1917, no less than 63,580 tons were exported for munitions.

DIRECTOR OF INDUSTRIES
Bengal

STATISTICS OF THE PRODUCTION OF CALCIUM NITRATE IN NORWAY BY THE ARC PROCESS.

Year	Production in metric tons		Consumption in metric tons (approx.)
	Calcium nitrate	Combined nitrogen[1]	Calcium nitrate
1907 .	1,601	208	215
1908 .	5,102	663	470
1909 .	11,953	1,554	970
1910 .	18.569	2,414	1,860
1911 .	13,152	1,709	1.967
1912 .	36,468	4,741	3,721
1913 .	73,214	9,518	5,500
1914 .	82,000	10,700	7,500
1915 .	48,000	6,200	9,500
1916 .	61,000	7,900	15,000
1917 .	72,000	9,400	36,500
1918 .	105,000	13,600	51,000
1919 .	109,000	14,200	45,000
1920 .	—	—	110,000

The Schönherr Arc Furnace. In 1905 Schönherr and Hessberger, working for the Badische Anilin und Soda Fabrik, devised a new type of arc furnace (Trans. Amer. Electrochem. Soc. 1909, 16, 131). Experiments with this furnace were carried out at Christiansand, in Norway, and extensive trials were made at Notodden with the object of deciding whether the new furnace possessed the advantages over the Birkeland and Eyde type which were claimed for it. As a result of this work the Rjukan I works was equipped partly with Schönherr and partly with Birkeland and Eyde furnaces, whilst the newest works, Rjukan II, is equipped throughout with the Birkeland and Eyde furnaces. By this time the Badische firm had severed its connection with the Norwegian company and turned its attention to the development of the Haber synthetic ammonia process.

The construction of the furnace (Elektrotechnische Zeit. 1909, 30, 365, 397) is seen in Fig. 6. The iron tube A contains at its lower extremity the electrode insulated from the rest of the furnace. It consists of a strong copper body, B, pierced through its axis and cooled with water. Through the axis passes an iron bar, C, which can be pushed forward as required, and constitutes the actual electrode from which the arc starts at the point D. All the wear comes upon this bar, which at the intense heat of the arc becomes covered with a layer of melted ferric oxide, which slowly evaporates. As this proceeds, the iron bar is gradually pushed forward, and its actual position can be observed through the peep-hole E. F is an igniting rod for starting the arc. The air enters the furnace as indicated, and at G passes into the iron tube through several series of tangential openings, situated one above the other, and regulated by means of the movable sleeve H. This device gives the entering air a rotary motion, which causes the arc once started from D to travel up the tube A, and the air current is so regulated that the arc ends in the upper water-cooled portion of the iron tube, somewhere between K and M, which portion of the furnace can be observed through the peep-holes N and O.

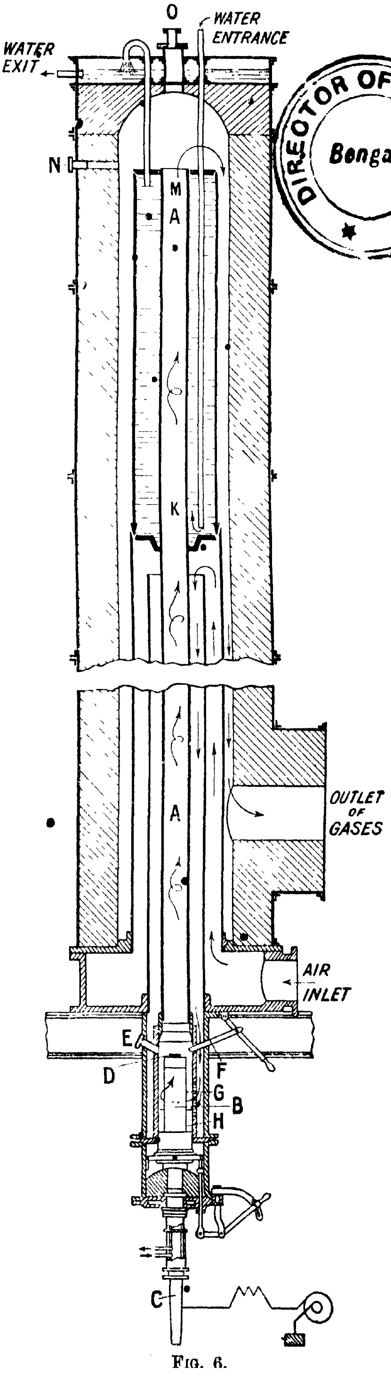


FIG. 6.

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[1] On a basis of 13 p.c. combined nitrogen in the nitrate.

Under these circumstances the arc burns as steadily as a candle flame The passage of the air through the furnace is indicated by the arrows, and it will be noticed that the incoming air is heated (to a temperature of about 500°) by the outgoing gases

The furnace is connected electrically to earth, so that any part of the apparatus can be handled with impunity, except only the insulated electrode.

The experimental furnaces at Christiansand (Fig. 7) utilised 600 h.p each at 4200 volts; although units taking 2000 h p. were considered possible, those recommended as a result of experiments took 750 h.p., requiring 40,000 cu. ft. of air per hour. They are, therefore, very much smaller than the latest Birkeland Eyde furnaces. The arc is then about 16 feet long, although Schönherr has recommended arcs 23 feet long.

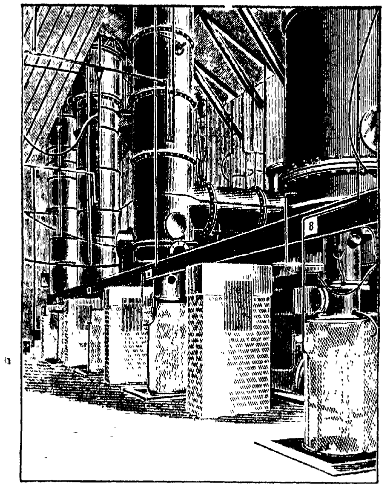

FIG. 7.

Experimental Schonherr Furnaces at Christiansand Works.

The gas leaving the furnace has a lower temperature, viz 800°, than that from the Birkeland-Eyde furnace, which materially reduces the efficiency of recovery of waste heat by boiler plant, but are said to be somewhat richer in oxide of nitrogen, viz. 2 p.c. as compared with 1·25–1·5. Very little information is available in connection with the Schonherr furnace; the output per kw. hr. is said to be about 5 p.c. higher than in the Birkeland-Eyde furnace, and the furnace is simpler in construction. Large quantities of cooling water are required, which are strongly heated and might be used in boilers. During the war Schönherr furnaces were installed in Germany on a restricted scale for the production of nitric acid.

The Pauling Arc Flame. In the production of this flame (Russ, Zeitsch. Elektrochem. 1909, 15, 544) the main iron water-cooled electrodes AA, Fig. 8, are bent into the shape of a **V**, and at the lowest point of the **V** (40 mm. wide) they form a vertical slot, through which are introduced narrow 'lighting knives,' B, B, which can be brought together by an adjusting arrangement, CC, until only separated by a few millimetres.

The arc is lighted at the narrowest portion of the spark gap. A high speed current of previously heated air is introduced into the **V** formed by the electrodes, through a nozzle, D, blowing out and broadening the arc, the flame so produced burning with remarkable steadiness from the electrical point of view, and in practice having a length of 1 metre. The furnace gases are cooled by so-called 'circulation air,' which is introduced sideways into the upper portion of the flame, at a lower speed than the main air current, thus exerting a suction effect on the flame, causing it to be drawn out, and further broadened. The gases leave the furnace at a temperature of 700°–800°, and were said to contain 1·5 p c. of nitric oxide. As operated by Dr. Rossi at Legnano, however, the furnace yields a gas containing only about 0·8 p.c. of NO

The Pauling furnace was originally installed by the Saltpetersaure Industrie Gesellschaft Gelsenkirchen, at a works at Patsch, near Innsbruck, where 15,000 h.p. are available. Twenty-four furnaces were used, each requiring 400 kw. at 4000 volts and about 21,000 cubic feet of air per hour. The results obtained led to the establishment of the Rossi works at Legnano, near Milan, using 12,000 h.p., which has more recently been extended to the extent of 6,800 h.p., and a small one at La Roche-de-Rame, in the south of France, producing 350 tons of nitric acid per annum.

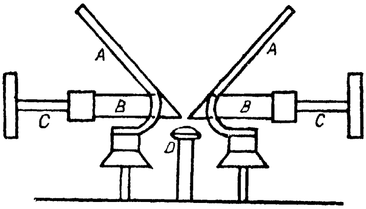

FIG. 8.

The original Pauling process gave unsatisfactory results in Italy, the yield never exceeding 23–25 grms. HNO_3 per kw. hr., as compared with about 60 in other processes. Investigations by Rossi appear to have shown that this low yield is caused by the action of finely divided oxide of iron carried away by the gases from the iron electrodes. This acted catalytically on the nitric oxide in the hot gases, bringing about its decomposition. It was found: (1) that the yield at the furnace was normal, but when the gas had cooled a considerable amount of fixed nitrogen had disappeared; (2) when the iron electrodes were replaced by those of other metals, this decomposition did not occur. Rossi (Eng. Pat. 23959, 1913) used electrodes of aluminium, preferably alloyed with other metals such as barium. Alumina, which is produced by disintegration, has no decomposing action on the nitric oxide; the alumina also forms a non-conducting coating on the inside of the furnace.

Pauling furnaces are used in much smaller units than other types. In the Rossi works the units take 500-600 kw., at a pressure of 5000 volts. In the new furnaces the electrodes are placed very close together at their point of convergence, and no auxiliary lighting knives are then necessary. A steam boiler is placed directly over the furnaces, to make use of the waste heat, the steam being used in concentrating the acid. It is proposed to install future furnaces inside boilers, and so use them as heating tubes.

The furnaces at Legnano are worked intermittently by off-peak power from the Milan Power Co. It is said that no difficulty whatever is experienced in starting up the furnaces, and this is an important factor when off-peak power is to be utilised, as would probably be the case if the arc process were adopted in Great Britain. The energy consumption is stated to be 1 kw. hr. per 74·4 grms. HNO_3 as acid and nitrite. This is a higher yield than that claimed for the Birkeland-Eyde process.

The Pauling furnace appears to be suited to small installations, whilst the Birkeland-Eyde or Schönherr probably has the advantage for large works.

The Moscicki Furnace. This type (Eng. Pat. 20497, 1903) is at present in operation only at Chippis, in Switzerland, where there are 12 furnaces, each of 1000 kw., of which two are in reserve. The furnace differs considerably in construction from those described above. Two concentric electrodes are used, the space between them being occupied by an arc which is caused to revolve under the influence of a powerful magnetic field with lines of force parallel to the common axis of the electrodes. The revolving arc practically fills the working space between the electrodes. The latter are water cooled, and have outlets for the gases. The pressure is 8000 volts, alternating current being used. The gases contain an average of 1·6 p.c. nitric oxide The output is stated as 438 kg. HNO_3 per kw. yr., which is decidedly low.

Other Furnaces. Besides those described, a number of other arc furnaces have been devised (*e.g.* by Guye, Scott (J. Soc. Chem. Ind. 1917, 771), and Island (U.S. Pat. 1316445)), but they have not yet been worked on a large scale. The Kilburn Scott furnace uses three horn-shaped electrodes at angles of 120°, a blast of air being projected through the space where the electrodes converge. A three-phase alternating current is used, at high voltage. Experiments with the furnace indicate that the yields are satisfactory, and the construction is simple. It has not yet, however, been operated under really technical conditions. Experience has shown that an increase in size of arc furnaces is often attended by a drop in efficiency, and the rather extravagant claims for special furnaces, based on laboratory runs, must be accepted with reserve.

The use of air enriched with oxygen in the arc process has been developed by the Société Nitrum of Zurich (F. Gros, Compt. rend. 1920, 170, 811; Ullmann, Enzyklopädie der techn. Chem., vol. 9, 654). A dry mixture of equal volumes of oxygen and nitrogen is circulated, in a closed system, only so much oxygen being supplied as is necessary for the final product (*e.g.* nitric acid). The gas and liquid in the absorption system, which is naturally much smaller than is necessary when air is used, are cooled to about 0°C. The gas leaves the furnace at 1500°C., containing 2·5-3·0 p.c. of NO. The oxygen, of 78 p.c. purity, is produced by a Linde machine of 1000 cu. m. per hour capacity, this being the largest size unit made, at a cost of 3 ctms. per cu. m. Three-phase furnaces of special design, with three arcs, are used, of 3000 kw. capacity, with water-cooled electrodes of special steel which last 72 hours in use. A mass of flame is formed, the air being blown tangentially into the furnace, and the flame is then suddenly chilled by passing the gases from the furnace, at a very high speed, through a double-walled water-cooled tube, from which they pass to a tubular boiler. The electrical equipment is complicated and expensive. Water absorption, of 95 p.c. efficiency, is used in a special apparatus. Nitric acid of 62 p.c. strength is obtained, the yield being 70-75 grms. per kw. hr. measured at the furnace. An installation at Bodio, in Switzerland, of 6000 kw. has been working since 1910. Liquid nitrogen peroxide is also made and stored in 80-ton aluminium tanks. It was liquefied by cooling the furnace gases in aluminium tubes with liquid ethane, which was cooled to —78° with light petroleum. A mixture of liquid NO_2 with a hydrocarbon forms an exceedingly violent explosive, which found some application in the war. A licence was granted in 1916 to a factory at Lauffenburg, Germany, for utilising 15,000 kw. Power is generated at 6000 volts, stepped up by transformers to 12,000-13,000 volts for the furnaces, each taking 3000 kw. Power is used for fixation only during the night. One kg. of N fixed as 62 p.c. acid costs 1 fr. 20 cts., with energy at just under 1 ct. per kw. hr. The yield is 70 grm. HNO_3 per kw. hr., and the cost of the acid is said to be cheaper than that made via the Haber process. A 60,000 kw. installation erected at Merseburg, cheek-by-jowl with the new Haber factory, was completely destroyed by an explosion (*cf.* also J. Soc. Chem. Ind. 1917, 36, 214). The Bodio works have also suffered from an explosion which occurred during the fractionation of an accidently formed mixture of NO_2 and petroleum (*see* J. Soc. Chem. Ind 1922, 41, 114 R).

Absorption of Oxides of Nitrogen in the Arc Process. An account of the absorption of the 1 or 2 p.c. of NO in the gases from the arc furnace, with the production of nitric acid or nitrates and nitrite, has already been given in connection with the description of the works at Soulom.

At Notodden there are three series of granite towers, 6 m. wide and 20 m. high internally, 5 towers in each series. Three of these are acid absorption towers and 2 are alkali absorption towers. The acid towers are 10-sided granite structures, the granite slabs being bound with iron rods. The towers have a capacity of 600 cu. m., and are filled with a packing of broken quartz, over which water or dilute nitric acid is circulated. The alkali towers are cylindrical iron towers of 700 cu. m. capacity, filled with broken quartz, over which sodium carbonate solution flows, which is converted into a mixture of nitrate and nitrite.

At Rjukan there are 32 granite absorption towers, each 34 m. high and 7 m. diameter, and weighing 2400 tons. These are fed with water to produce nitric acid, and the later towers with soda to form nitrite. The products made at Notodden are calcium nitrate, sodium nitrate, ammonium nitrate, and sodium nitrite. At Rjukan, concentrated nitric acid is made in addition.

The products are transported from Rjukan, 47 km. by tramway, 31 km. by steam ferry, and then arrive at Notodden.

In the Legnano works of Rossi, using the Pauling process (*see* above), there is an empty oxidation tower of 70,620 cubic feet capacity, 5 acid towers, each 65·6 feet high and 16·4 feet diameter, and 4 iron alkali towers, each 72 feet high and 11·5 feet diameter. The strongest acid is 23–25 p.c. HNO_3, and 20 p.c. of the absorbed gas is recovered in the alkali towers. The loss is only 1 p.c.

The gargantuan proportions of the absorption system used in an arc plant cannot fail to strike the reader. It forms a very expensive part of the plant. It would seem possible, by careful consideration of the factors of oxidation and absorption, to effect some economy in this direction. Dr. Parker, by applying the formulæ given on p. 594, has shown that, by a suitable arrangement of oxidising and absorption spaces, the 13,030 cu. m. of tower space used at Pierrefitte might be reduced to about 9000 cu. m., with an increased efficiency of absorption of 3 p.c. The reduction of packed space would also reduce the expense and weight of the plant. There is room for experiments in this direction, since the present method is purely empirical. Experiments at Angoulême indicated that three towers, 18 inches diameter and 15 feet high, with scientific arrangement, effect the same absorption as one of the usual granite towers 60 feet high, weighing 260 tons and costing £4000. The first tower system would cost about £150.

The reactions taking place in the absorption towers are still somewhat obscure. The primary reaction is the absorption of nitrogen dioxide with the formation of equivalent amounts of nitric and nitrous acids:

$$2NO_2+H_2O=HNO_3+HNO_2, \text{ or}$$
$$2N_2O_4+H_2O=2HNO_3+N_2O_3.$$

So far as is known there is no difference in the products with NO_2 and N_2O_4, although there is some evidence that the rates of absorption are different in the two cases. With increasing concentration the nitrous acid becomes unstable, and decomposes, the greater portion being eliminated. The exact mechanism of the elimination of the nitrous acid is very little understood. J. R. Partington and L. H. Parker, in a paper on the Theory of Absorption Towers for Nitric Acid (J. Soc. Chem. Ind. 1919, 38, 75 T) have considered the absorption of oxides of nitrogen in towers.

The efficiency of a tower system will depend on two factors:—

(1) *The rapidity and completeness of absorption.*—This may be determined by the weight of soluble gas extracted per minute per cubic foot gross tower space, and the overall percentage absorption.

(2) *The concentration of the solution produced.*—This factor, which is always kept in mind in designing towers for condensing hydrochloric acid, appears to have been largely overlooked in nitric acid towers. It is, however, of considerable importance, as the costs of handling, storing, and working up 30 p.c. nitric acid are obviously much greater than the corresponding figures for 50 p.c. acid.

Rapidity and completeness of absorption.—The rapidity may be stated in the form of the number of pounds of NO_2 absorbed per cubic foot gross tower space per minute. The completeness may be estimated from the overall efficiency of absorption, *i.e.* the percentage of oxides of nitrogen removed from the gases entering the towers during their passage through the towers.

The weight in lbs. of nitrogen dioxide absorbed in 1 minute per square foot of acid surface, which we shall call the *absorption coefficient*, depends on the partial pressure of NO_2 in the gas; the partial pressure of oxygen in the gas; the concentration of the acid used for absorption; the temperature; the turbulence of the liquid and of the gas; the amount of oxidation space allowed for the NO produced during the absorption; and the rate of renewal of liquid surface, *i.e.* the acid flow through the tower.

The dependence on the partial pressure of NO_2 is sufficiently evident on comparing the tower capacity used for dilute gases produced in the arc, with that for the much richer gases obtained by denitration:—

Gas	P.c. NO_2 in gas	Cub. ft. gross tower space per lb. NO_2 per min.
Arc . .	1	5000
Denitrator .	20	200

The dependence on the strength of acid used for absorption is shown approximately as follows:—

P.c. strength of acid used for absorption	Rate of absorption
0	1·00
10	0·99
20	0·95
30	0·90
40	0·80
50	0·70
60	0·55
65	0·32
68	0·00

(*see* Foerster and Koch, Zeitsch. angew. Chem. 1908, 2161, 2209; Foerster, Burchardt, and Fricke, Zeitsch. angew. Chem. 1920, 33, 113, 122, 129; Hall, Jacques, and Leslie, J. Soc. Chem. Ind., 1922, 41, 285 T).

There is evidence of a maximum speed of absorption in 10 p.c. acid.

Elimination of nitrous acid.—The primary reaction in the absorption of nitrogen dioxide in water is presumably the formation of 1 molecule each of nitric and nitrous acids. The elimination of the nitrous acid from the liquid now follows, because it is found that the acid produced in absorption towers rarely contains more than about 0·3 p.c. of HNO_2.

The exact mode of elimination of the nitrous acid from the liquid is not at present definitely settled, and there are different theories on the subject:

(1) *The nitric oxide theory.*—According to this the nitrous acid decomposes according to the equation: $3HNO_2 \rightleftarrows HNO_3+2NO+H_2O$ (Lewis and Edgar, J. Amer. Chem. Soc. 1911, 33, 292; Ssaposhnikoff, J. Russ. Chem. Soc. 1900, 32, 375; 1901, 33, 506; Burdick and Freed, J. Amer. Chem. Soc. 1921, 43, 518).

In the presence of an atmosphere of nitric oxide this reaction reaches an equilibrium when nitrous and nitric acids are present together in the solution. In actual tower practice, however, there is an excess of oxygen and of indifferent gas. Both these factors will tend to reduce the nitrous acid concentration in the solution; the first by removing the supernatant NO, with formation of NO_2, which then re-dissolves, and the second by reducing the partial pressure of the NO. There is no doubt that, in so far as this reaction plays a part in the removal of HNO_2, both these factors are of influence.

(2) *The volatilisation theory.*—Nitrous acid in aqueous solution above a certain strength exhibits a marked blue colour, owing to partial dissociation with the formation of N_2O_3. The N_2O_3 tends to escape from the solution owing to its volatility.

(3) *The oxidation theory.*—In absorption towers, where excess of oxygen is present, the reaction $2HNO_2+O_2=2HNO_3$ undoubtedly takes place in solution, and probably to a still greater extent in the Pohle lifts, where a very efficient churning together of the liquid and the air used for working the lifts occurs. The use of oxygen instead of air in working the lifts would greatly increase this oxidising action.

Under average conditions it may be assumed that the elimination of nitrous acid proceeds at a rate sufficient to allow it to be neglected in considering the rate of solution of the oxides of nitrogen.

Oxidising space in towers.—Although some of the nitrous acid produced in the absorption towers is eliminated in solution by oxidation, as described above, the greater part reappears in the gas phase in the condition of nitric oxide, arising from the reactions:

$$(a)\ 3NO_2+H_2O=2HNO_3+NO$$
$$(b)\ 2NO+O_2=2NO_2.$$

Equation (a) appears to be the sum of two separate reactions, involving the intermediate formation of nitrous acid. Reactions (a) and (b) constitute a cycle, in which out of three mols. of NO_2 taken, two are absorbed, and one remains for further absorption. One-third of the NO_2 therefore remains after each cycle. Thus, after 4 cycles, about 99 p.c. of the oxides are absorbed.

The regeneration of NO_2 by reaction (b) is not, in ordinary tower practice, carried out under ideal conditions, because this reaction appears to take place in two stages:

$$2NO+O \rightarrow N_2O_3 \text{ (rapid)}$$
$$N_2O_3+O \rightarrow N_2O_4 \text{ (slow)}.$$

This is practically true because, although N_2O_3 does not appear to have an individual existence (except in traces) under the conditions of working (Lunge and Berl, Zeitsch. angew. Chem. 1907, 20, 1716; Bodenstein, Zeitsch. Elektrochem. 1918, 24, 185), yet the mixture of equal molecules of NO and NO_2, if presented to an absorbing medium (*e.g.* sulphuric acid, or caustic soda), is rapidly absorbed as N_2O_3. The equilibrium

$$NO+NO_2 \rightleftarrows N_2O_3$$

is therefore very rapidly displaced to the right. If this mixture is brought in contact with water it is absorbed as nitrous acid:

$$H_2O+NO+NO_2 \rightleftarrows N_2O_3+H_2O \rightleftarrows 2HNO_2.$$

The cycle of reactions, under these conditions, will now be as follows:—

$$(1)\quad 3N_2O_4+2H_2O=4HNO_3+2NO$$
$$(2)\quad 2NO+\tfrac{1}{2}O_2=N_2O_3$$
$$(3)\quad N_2O_3+H_2O=2HNO_2$$
$$(4)\quad 3HNO_2=HNO_3+2NO+H_2O.$$

It can be shown that, with these reactions, it is necessary to go through at least 10 cycles to produce the same effect, if N_2O_3 is produced in the re-oxidation, as with 4 cycles in which the gas presented to the liquid is fully oxidised N_2O_4. This will very much increase the tower space required. Patents have been framed to obviate this formation of N_2O_3, by removing the gas after each contact with water, and allowing it to be fully oxidised before again bringing it into contact with water or acid (see below). The actual conditions obtaining in towers are, however, more advantageous than would appear at first sight, for the following reasons: (1) The oxidation in the free space will proceed beyond the stage N_2O_3, and a portion at least of the gas will be in the state of fully oxidised N_2O_4 after each cycle. (2) Opportunity for complete oxidation will occur in the connecting pipes between the towers (if these are provided, as should always be the case).

The complete oxidation of nitric oxide by atmospheric oxygen, in the case of dilute gases, is a slow process, and this reaction is the chief source of difficulty in all nitrogen fixation processes in which nitric oxide is the primary product. Chemical engineers do not seem to have an adequate conception of the kinetics of this reaction, and many faulty plants have in consequence been erected, only to require subsequent modification at great expense. It may be said that, for gas containing 2 p.c. of NO, a time of contact of not less than 2 minutes is required for adequate oxidation of this gas before subsequent absorption is attempted. In this case 90 p.c. of the NO will be oxidised to NO_2. A useful discussion of this process is given by G. W. Todd, in Physical and Chemical Data of Nitrogen Fixation, H.M. Stationery Office, 1919.

Mist formation in towers.—An important phenomenon which makes its appearance during the absorption of oxides of nitrogen in water is the formation of a white mist, which is carried away by the inert gas passing through the towers, and appears in the exit gas. The mist is found to consist of quite strong nitric acid in the form of droplets, which are formed as soon as the oxides of nitrogen enter the train of absorption towers, *i.e.* in the strong acid tower, and pass unaltered and uncondensed through the remaining weak acid towers.

In the absorption of gases from arc furnaces, the gases coming from the water towers contain a considerable quantity of acid mist, which normally passes into the soda towers and is there absorbed as sodium nitrate. If soda towers are not used, this mist escapes condensation, and even with soda towers the absorption is incomplete. By means of electrical precipitation apparatus it is possible to condense the mist to 35 p.c. nitric acid, *i.e.* acid corresponding with that in the first tower.

It will be evident from the above discussion that the problems to be solved in the design of absorption towers for nitric acid are much more complicated than those involved in such cases as the absorption of hydrochloric acid. A complete theory is lacking, and the experimental data are scanty. On the basis of results obtained by E. K. Rideal (J. Ind. Eng. Chem. 1920, 12, 531), J. R. Partington and L. H. Parker (*l.c.*) have deduced some practical rules and formulæ which represent about all that is known at present of this matter.

A simple formula can be deduced which is found to give good results in actual tower practice. If v is the total volume of the tower in cubic feet, k the number of square feet of surface exposed by the packing per cubic foot, V the velocity of flow of gas through the tower in cubic feet per second, and K a coefficient which measures the rate of absorption and has been tabulated from experimental results for various concentrations of gas and acid and different temperatures, then: $\log_e c_0/c_1 = Kkv/V$, where c_0 and c_1 are the concentrations of NO_2 in the gas entering and leaving the tower respectively in lbs. per cubic feet.

The following values of K and k are most generally applicable; for the complete tables, and examples of calculation applied to tower design, reference must be made to the original paper.

VALUES OF $K \times 10^2$.

P.c. NO_2 in gas	50° C.				40° C.				30° C.			
P.c. HNO_3 in acid	1	4	8	10	1	4	8	10	1	4	8	10
5	1·97	2·14	2·83	3·00	2·91	2·59	2·83	2·89	2·28	2·39	2·73	2·83
10	2·59	2·55	2·91	3·00	2·44	2·53	2·85	2·93	2·12	2·39	2·78	2·88
16	1·57	1·73	2·47	2·67	2·20	2·41	2·71	2·78	1·96	2·32	2·67	2·75
25	1 10	1·18	1·98	2·23	1·97	2·01	2·30	2·38	1·81	2·26	2·47	2·52
37	0·63	0·67	0·91	1·06	1·73	1·49	1·77	1·85	1·65	1·83	2·28	2·36
42	0·471	0·471	0·69	0·85	1·49	1·28	1·56	1·65	1·57	1·63	2·18	2·31
52	0·20	0·18	0·44	0 61	1·18	0·85	1·22	1·37	1·41	1·24	2·06	2·26

COMPARISON OF VARIOUS TYPES OF TOWER PACKING.

Packing	Exposed area of unit, sq. in.	Volume of unit, cub in.	No of packing units per cub ft. tower space	Total surface of packing units in sq ft per cub ft tower $=k$	Total volume of packing units in cub. ft. per cub ft tower	P c. free space	P.c. gross space occupied by packing	Sq. ft. exposed per cub ft. gross space to leave 80 p.c. free space
Small Raschig rings	5·46	0·368	2,130(1) 1,700(2)	80·6 64·5	0·452 0·362	54·8 63·8	45·2 36·2	35·6
4-Point star [1]	5·81	0·597	545	22	0·188	81·2	18·8	23·4
Guttmann balls	23·4	3·05	75	12·2	0·132	86·8	13·2	18·4
Concentrics	46·5	6·1	152	49	0·538	46·2	53·8	18·3
Large rings and concentrics	93·6	13·15	64	41·6	0·489	51·1	48·9	17·1
Large rings	47·1	7·07	64	20·9	0·262	73·8	26·2	16·0
Rings and nodules	Ring 47·1	7·07	14·8	4·85	0·0606	89·6	10·4	9·33
	Nodule 11·1	2·91	25·7	1·98	0·0432			3·78
				6·83	0·104			13·11

Many proposals have been made to carry out the absorption of oxides of nitrogen without the use of towers, or in specially arranged towers. In some of these the necessity for providing oxidising space for the gas is recognised. Häusser (Eng. Pat. 7419, 1914) makes provision for re-oxidation of the NO produced in the interaction between NO_2 and water by causing the gas to traverse a long path after each absorption. Engels and Durre (D. R. P. 229096, 1908) pass gases containing not less than 50 p.c. of N_2O_3 through a series of towers fed with water and add air in portions to each tower. Naville and Guye (Eng. Pat. 6155, 1908) allow oxides of nitrogen containing fully oxidised NO_2 to react with water until about two-thirds of the oxides are removed. The residual gas, containing NO, is then dried, say, by cooling, and allowed to reoxidise completely in an empty chamber out of contact with water. The fully oxidised gas is again brought in contact with water until another two-thirds is absorbed, and the process repeated. Meister, Lucius and Bruning (Eng. Pat. 19032, 1911) use compressed oxygen instead of air in operating acid elevators, the gas from the elevators being introduced into the towers. The Norsk Hydro (Eng. Pat. 100099, 1917) effect absorption under pressure, when the volume is reduced proportionally to the square of the pressure (*cf.* Naville and Guye, Fr. Pats. 385569 and 385605, 1908, in which absorption of arc furnace gas under pressure is said to give 95 p.c. HNO_3 directly). Bergius (D. R. P. Anm. B. 53617) compresses oxides of nitrogen to 25 atm., adds steam, and expands suddenly into a chamber, when nitric acid is said to be obtained. An interesting method is described by Moscicki (Eng. Pat. 17355, 1911), who causes the liquid to pass down the towers intermittently, so that the packing is periodically wetted. The absorption apparatus comprises rectangular chambers built into one block, the dividing walls being pierced with small holes. Alternate chambers are packed and empty. The width of each chamber is only 15-30 cm., and the gas flows at the rate of about 4 cm. per second horizontally through the apparatus. The absorbing chambers are flooded intermittently with liquid, which is allowed to drain off, and elevated to the top of the next chamber in opposition to the motion of the gas.

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[1] A form of tower packing designed by J. R. Partington and L. H. Parker.

(1) Thrown into tower. (2) Stacked in tiers.

An alternative method of absorption is that proposed by A. Schloesing (Fr. Pat. 460328, 1912), in which quicklime in the form of briquettes is treated with the hot furnace gases for some days. Calcium nitrate and nitrite are first formed, but under the influence of the air and nitrous gases the nitrite is ultimately completely converted into nitrate, obtained in a solid form. In this connection the observations of Oswald (Ann. Chim. 1914, [ix] 1, 32) are of interest. This experimenter found that on passing nitrogen dioxide over hot lime, a loss of 20 p.c. of combined nitrogen occurred. Oswald represents this by the equation: $2CaO+5NO_2=2Ca(NO_3)_2+N$. According to Schloesing, with the very dilute gases from arc furnaces, there is no loss of combined nitrogen. Possibly the more dilute gas used by Schloesing, and his special preparation of the lime, may account for the different result. The inventor lays great stress on the preparation of the lime briquettes. Quicklime obtained by burning soft chalk is slaked, the hydrate is pressed into briquettes, and the latter are dehydrated at as low a temperature as possible, say 500°. The gas must be dry and free from carbon dioxide, and is passed over the lime in lagged iron retorts at 300°-400°. J. R. Partington and E. Whitworth find that, with specially prepared lime, loss of nitrogen does not occur, and complete conversion to nitrate may be attained, with dilute gases. Trials of the process on a fairly large scale were made at Notodden, and the results were stated to be satisfactory. The product contains about 14 p.c. of combined nitrogen, and 12-13 p.c. of free lime. The process is not worked at present.

THE OXIDATION OF AMMONIA.

In 1788 the Rev. I. Milner found that ammonia gas is oxidised to nitric acid when passed over heated manganese dioxide, and Black (Lectures on Chemistry, 1803, pp. 245, 455; Nature, 1922, 109, 137) states that the process was used by the French on the large scale during the Napoleonic wars for the manufacture of saltpetre. This observation was followed by the better known researches of Kuhlmann, of Lille, who in 1839 (Liebig's Annalen, 1839, 29, 280) observed that when a mixture of ammonia and air is passed over platinum sponge heated to about 300° the platinum continues to glow and red fumes of oxides of nitrogen are formed. A slight reaction was noticed when the gas was passed through an empty heated porcelain tube. Kuhlmann also found that platinum black is less efficient than platinum sponge, copper, nickel, iron, and copper hydroxide being still less active; he also found that cyanogen and hydrocyanic acid are very readily oxidised—an observation confirmed by Moldenhauer and Wehrheim (Zeitsch. angew. Chem. 1914, 27, 334). Kraut (Annalen, 1865, 136, 69) noticed that red fumes, with intermittent explosions, result when a hot platinum spiral is hung inside a flask containing ammonia solution through which oxygen is passed. Chromium oxide and chromates were proposed as catalysts for the oxidation of ammonia by Aubertin (Eng. Pat. 1181, 1871); du Motay (Eng. Pat. 491, 1871) used manganates, permanganates, bichromates, and alkali plumbites. Sodium manganate was also used by Schwarz (Dingl. poly. J. 1875, 218, 219); Marston (Eng. Pat. 19074, 1900) used copper. The formation of fumes of ammonium nitrite and nitrate on passing ammonia and air over platinised asbestos heated to redness was described by Warren (Chem. News, 1891, 63, 290). The yield of oxides of nitrogen with platinised asbestos as catalyst was investigated by Schmidt and Bocker (Ber. 1906, 39, 1366); the yields with various catalysts were determined by Neumann and Rose (Zeitsch. angew. Chem. 1920, 33, 41, 51). Meninghini (Gazz. chim. ital. 1912, 42, i, 126; 1913, 43, i, 81) and Reinders and Cats (Chem. Weekblad. 1912, 9, 47) investigated oxides as catalysts. The use of platinised glazed porcelain was patented by Schick (Eng. Pat. 13954, 1907); this is described as having a longer life than platinum sponge (*see also* Taliani, Giornale di Chimica Industriale ed Applicata, 1921, 408). F. Bayer & Co. pass ammonia and air at 600°-700° over a catalyst containing oxide of iron and 'promoters' (Eng. Pat. 18594, 1903). The Badische Co. propose the use of oxides of the iron group, the catalyst being in the form of lumps or pieces (Eng. Pats. 13687, 1914; 7651, 13298, 1915; *cf.* Partington and Rideal, Eng. Pat. 135224, 1917; Maxted, J. Soc. Chem.

Ind. 1917, 36, 777). The use of oxide of iron with bismuth oxide (Eng. Pat. 13848, 1914), or tellurium (Eng. Pat. 13297, 1915), or platinum and lead (Eng. Pats. 13297, 13299, 1915) is proposed by the same firm. Frank and Caro (D. R. P. 224329) advise ceria and thoria (which J. R. Partington has found inefficient); Jones, Morton, and Terziev use plumbites of aluminium, zinc, or cadmium (U.S. Pat. 1037261, 1912); Parsons (U.S. Pat. 1239125, 1917) mentions lead oxide supported on bone-ash at 1000°. This list does not exhaust the catalysts proposed.

The conditions for obtaining a practical yield with platinum were investigated by Ostwald and Brauer in 1900; the method is described in Eng. Pats. 698, 8300, 1902, and 7909, 1908; a German patent was not granted on account of the prior work of Kuhlmann. It was found that the gas must be passed rapidly over the catalyst, otherwise the ammonia is largely burnt to elementary nitrogen:

$$2NH_3+3O_2=2N_2+6H_2O.$$

Under suitable conditions, however, well over 90 p.c. of the ammonia may be oxidised to nitric oxide: $4NH_3+5O_2=4NO+6H_2O$. The mechanism of the reaction has been discussed by Mendeléeff and others; hypothetical intermediate compounds such as $N(OH)_3$ have been postulated, but nothing definite is known beyond the fact that nitric oxide is the first ascertainable product of the oxidation.

A technical plant based on Ostwald's investigations was erected in 1909 at the works of the Lothringian Colliery Co. at Gerthe, near Bochum, which produced more than 1800 tons of ammonium nitrate per annum (C. Trade J. 1915, 56, 553). The patents were taken over by the Nitrogen Products Co., who erected factories at Vilvorde in Belgium and Dagenham in England. The original Ostwald process has been in operation for many years and, with suitable precautions, gives yields of 85–95 p.c. of the theoretical.

The ammonia oxidation process in the Ostwald form was largely used in France during the war, the ammonia being derived from cyanamide. The first works were installed at the Poudrerie nationale d'Angoulême. Carbide was imported from Switzerland and converted into cyanamide, nitrogen being obtained by the Claude process at Martigny, Notre-Dame de Briançon, and especially Bellegarde. From 2650 to 3500 tons of cyanamide per month were delivered at Angoulême. The first oxidation plants were operating in the autumn of 1916, and the whole were in operation in 1917. In 1917 it was decided to erect factories for making 500 tons of nitric acid and 150 tons of ammonium nitrate per day by the oxidation of ammonia. This programme required 800 tons of calcium carbide per day and 125,000 kw. Water power of the Pyrenees, Central France, and the Alps, and even central steam power plants at Nanterre and Carmaux were brought into requisition. The most important works was at Lannemezan (50,000 kw.), and new oxidation works were installed at Toulouse, Bassens, Sorgues, and Saint-Chemas. Toulouse and Bassens had begun to operate at the armistice, the others were nearly finished. These works would have supplied all requirements in nitric acid and ammonium nitrate.

The Ostwald converter consists of two vertical concentric tubes, acting as a heat exchanger. The heat evolved in the reaction raises the temperature of the gases, which pass down the inside of the inner tube. The heat is transmitted through the walls of this tube to the mixture of air and ammonia, which passes up the annular space between the tubes to the catalyst, which is placed at the top of the inner tube. The temperature of the catalyst is thus maintained at 800°–830° without heating from outside. The external tube is of iron, enamelled on the inside, the inner tube being of nickel, 3·5 m. long, 63 mm. diameter, and 1 mm. thick. The iron tube is 100 mm. internal diameter and is only 3·25 m. long, so that the nickel tube protrudes below 25 cm. This is prolonged by an aluminium tube, in which the gas cools to 260°–270° before passing into a large aluminium main collecting the products of several converters. The iron tube is lagged outside to hinder radiation.

The catalyst is prepared by taking two strips of platinum foil, 2 cm. wide and 0·01 mm. thick, crinkling one into ridges 1 mm. apart, laying this on the other flat strip, and rolling the two into a circular pad 65 mm. diameter, weighing 50 grms. The appearance of the catalyst then resembles the corrugated cardboard used for packing. At the top of the nickel tube and inside it are lugs, on which the roll of platinum rests. The outer iron tube is closed at the top by a hinged lid, with a mica inspection window through which the temperature of the catalyst may be observed. The activity of the platinum increases rapidly with use for some hours. It then slowly falls off and the catalyst requires renewal after three months. The platinum when taken out is found to be encrusted with dust, changed by impurities in the gas, or crystallised by the high temperature used. The activation of the platinum depends on a peculiar physical change (Rideal and Taylor, Catalysis, 1919, p. 97); the metal swells up into microscopic effloresccences, probably owing to solution of gas and subsequent expulsion.

Each converter unit produces 100 kg. nitric acid per 24 hours. The mixture of air and ammonia should contain about 8·5 p.c. of ammonia by volume. The proportions of air and ammonia may be determined by Venturi meters; before passing to the converter the two gases should be thoroughly mixed by passing through a tower with baffles or otherwise. The gas should also be filtered from dust, since oxide of iron acts very prejudicially on the catalyst.

At the Angoulême works there are 864 converters, arranged in three batteries of 6 rows of 48 units. The appearance of the converter house is reminiscent of a small forest. The ammonia gas is taken from a balancing holder of 300 cu. m. capacity by a 3 h.p. fan, the air is introduced by a 17 h.p. fan.

At the newer works at Bassens the air is taken in by suction through filters composed of thin rectangular boxes with flannel sides by means of two blowers delivering 7000 cu. m. per hour each. The air and ammonia gas are mixed in a vertical cylindrical iron mixer, 6 feet in diameter and 20 feet high, containing baffle plates, with two inlets placed tangentially at the bottom and an outlet at the top. The mixture contains 1 vol. NH_3 to 11 vols. air.

The converters are arranged on a floor above in 8 groups of 6 to form a battery:

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000000 000000 000000 000000

Each half of the battery has its own inlet and outlet mains. Twelve batteries of 48 units are arranged in one house, and 12 in a second house, each being served by a separate gasholder for ammonia.

The oxidised gas from each main coming from 24 converters enters by aluminium mains at about 200°C. 2 large U-tubes of silicon-iron, 18 inches diameter and 20 feet high, with 2 vertical outlets below. These tubes are cooled by a shower of water and the gas leaves at 80°C. It then passes to a series of 6 pottery U-tubes, about 18 inches diameter, placed in a water-bath with partitions to cause circulation of cooling water. Inside the U-tubes are vitreosil tubes closed at the bottom, acting as Hough's condensers, about 6 inches diameter and 16 feet long. Beyond these 6 U-tubes are 17 U-tubes, with internal cooling but exposed to the air. The water from the internal coolers of these passes to the trough of the first 6 tubes. The outlets from 4 batteries of tubes are joined in a rectangular trough of volvic lava, from which a single 24-inch pottery main leads the gas, cooled to 40°C., to a set of 6 absorption towers, 1 set of towers to 4 semi-batteries of 24 converters each, or 36 towers in all. Preceding each set of 6 towers are 4 empty oxidation towers in parallel, consisting of stoneware pipes, 18 inches diameter and 20 feet high. Owing to the heat of oxidation of the NO the gas leaving these towers is still at 40°C.

The absorption towers are of acid-resisting brick laid in silicate and sand mortar with iron strengthening bands. They are 4 m. internal diameter and 12·5 m. high. Joints are made with a soft mixture of asbestos, sulphur, and tallow. The gas passes into the bottom of each tower, down through an internal pottery pipe of 12 inches diameter to the bottom of the next tower. The packing is of quartz lumps, all the same size, 6 inches diameter. The gas pressure is 6 to 7 cm. of water at the entry to the towers. Acid is circulated in each tower by two Kestner automatic montejus per tower, delivering to the tops of the towers through aluminium pipes 2 inches diameter. The circulation of acid per tower is 5000 litres per hour. Towers 1 to 3 are cooled by passing the acid leaving them in a shower over a battery of glass tubes enclosed in a box of volvic lava with cold water running through the tubes. The reaction is intense in the third tower. The final acid is 33°Bé. The exit gas from the towers contains 4 grms. NO per cu. m.

The process of ammonia oxidation in which platinum is used as a catalyst has been considerably improved in recent years. The improvements are mainly in the direction of using platinum wire gauze instead of foil, and in replacing the nickel tubes, with a small output per unit, by cheaper and more convenient converters of aluminium or enamelled iron of much greater output per unit or per gramme of platinum.

The use of a single layer of electrically heated platinum gauze as a catalyst for the oxidation of ammonia was described by Frank and Caro (*see* Schuphaus, Metall und Erz, 1916, 13, 21) and by Landis (U.S. Pats. 1193796 to 1193800, 1916; Chem. & Met. Eng. 1919, 20, 470; on the construction of catalysts, *see* Oxidation of Ammonia, Munitions Inventions Department, Stationery Office, 1919; and A. A. Campbell, J. Ind. Eng. Chem. 1919, 11, 468).

The basis of all the recent improvements is to be found in the patent of Kaiser (Eng. Pats. 20325, 1910; 24035, 1911; D. R. P. 271517, 1914), who proposed the use of several superposed fine platinum or iridium gauzes in close contact, the mixture of air and ammonia gas being preheated, before passing to the catalyst, to 300°–400°. In this way a very rapid stream of gas may be passed through the apparatus and the output correspondingly increased.

In March 1917 J. R. Partington, in the course of experiments carried out for the Munitions Inventions Department, found that two platinum gauzes could be used, the lower one heated electrically and separated from the upper gauze by silica rods of small diameter. There was no marked improvement in the yield if more gauzes were added. Unless electrical heating or preheating of the gases is used the yield drops from 92–95 p.c. to about 85 p.c. even if four gauzes are used. The question of using gauzes in close contact, or slightly separated as in the above type of catalyst, has been much discussed. So far as experiments go there appears to be little difference, although the separated gauze type has recently been claimed to be more efficient (Perley, J. Ind. Eng. Chem. 1920, 12, 5, 119; Met. & Chem. Eng. 1920, 22, 125).

The size of the modern converters is very small in comparison with the output attained. Thus, a converter of cross-section 4 inches by 6 inches, with two gauzes, is sufficient to supply all the oxides of nitrogen required to replace the nitre pots in a large chamber plant. This is a convenient size for a unit, although larger sizes, with 1 or 2 square feet cross-section, have been operated. The output of 16 kg. HNO_3 per grm. platinum per 24 hours corresponds with an output of 1·5 tons HNO_3 per square foot converter cross-section (*i.e.* 2 square feet total *gauze* area) per 24 hours (J. Soc. Chem. Ind. 1918, 37, 337 R). For further details the reader is referred to the pamphlet on The Oxidation of Ammonia Applied to Vitriol Chamber Plants, H.M. Stationery Office, 1919.

A much higher rate of conversion has been attained in the most recent type of converter protected by J. R. Partington (U.S. Pat. 1378271, 1921). This contains 2 gauzes in contact, and the arrangement is otherwise the same, but the air was replaced by oxygen. Pure oxygen and ammonia gas form dangerously explosive mixtures until the ratio 1 vol. NH_3 to 3·5 vols. oxygen has been exceeded. But by mixing steam with the gases to damp down the explosion, and preheating to 500°, an almost quantitative conversion is obtained. The correct proportion of steam is formed by volatilising concentrated ammonia liquor (sp.gr. 0·88) completely in a current of oxygen sufficient to oxidise the ammonia completely to nitric acid. The products of combustion may then be condensed directly by cooling to fairly concentrated nitric acid, without the necessity of using the absorption towers required in the ordinary process. In view of the large amounts of oxygen obtained as a by-product in the preparation of nitrogen from the air by the rectification process, this method of oxidation seems to offer special advantages.

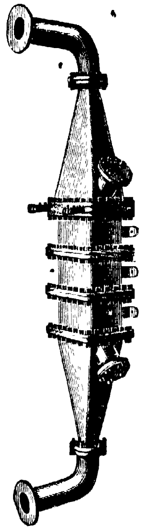

FIG. 9.

Ammonia Oxidation Converter

(*From Partington's 'Textbook of Inorganic Chemistry'* (*Macmillan & Co., Ltd.*))

The Munitions Inventions Department apparatus is shown in Fig. 9. It consists of a top and bottom cone (Fig. 10), with rectangular body pieces between, all in cast aluminium ¼ inch thick. Three body pieces are shown, but later experiments have shown that two, or even one, will suffice. The area inside is 4 inches by 6 inches. The pieces are provided with flanges, ¾ inch wide to facilitate bolting together, and perforated baffles of sheet aluminium are inserted between the body pieces, except at the junction between the top cone and body piece, which is occupied by a special catalyst (Fig 11) of two layers of platinum gauze, of pure platinum wire 0·0025 inch diameter, woven in uniform mesh with 80 strands to the linear inch.

The air and ammonia mixture passing to the converter, in the proportion of 1 vol. of ammonia to 7·5 vols. of air, is most conveniently obtained by blowing air through 25 p.c. pure ammonia liquor in a coke tower (Fig. 12), and driving off the ammonia by admitting a little steam at the base of the tower. Before entering the converter, the gas must be filtered, as traces of oxide of iron, present in dust, 'poison' the platinum and render it inactive.

The converter is started by heating the gauzes electrically, or with a Bunsen torch inserted beneath the catalyst. When reaction begins, it continues uninterruptedly without external heating. It is desirable to take out the platinum gauzes about once every two or three months, and clean them by boiling with concentrated hydrochloric acid. After six or eight months' use the platinum begins to disintegrate, and is replaced by a new gauze. Perfectly new gauze is not very active, but rapidly becomes activated after a day's use. Activated gauzes may be stored in a place quite free from dust.

The output per square foot of catalyst surface (2 gauzes) is equivalent to 1·5 tons of nitric acid per 24 hours. The gases from the converter are cooled in silica S-pipes exposed to air, and may then pass directly to the Glover tower or other part of the vitriol plant.

An improvement in the yield is attained by preheating the gases to about 400°–600°C. before the converter.

Enamelled iron converters, made by the Cannon Iron Foundries, Deepfields, Staffs., have also proved entirely satisfactory. A recent type of converter is described by C. S. Imison and W. Russell (J. Soc. Chem. Ind. 1922, 41, 37 T), and is used by the United Alkali Co. The gases are preheated by utilising the heat of the reaction itself. The converter is of iron, protected by enamel or by painting with sodium silicate solution and barium sulphate. This type of apparatus is a distinct improvement on other designs.

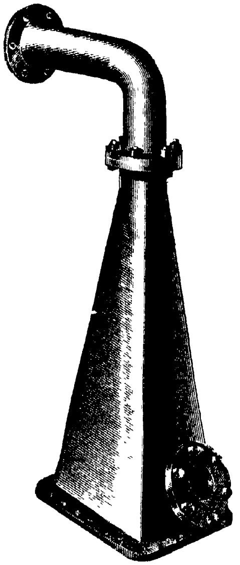

FIG. 10.

Cone of Ammonia Oxidation Converter.

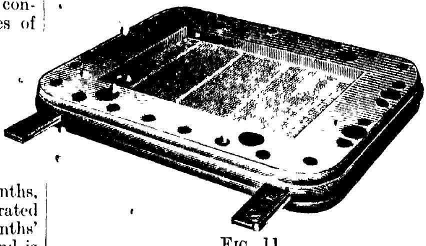

FIG. 11.

Catalyst for Ammonia Oxidation.

Parsons and Jones (J. Ind. Eng. Chem. 1919, 11, 541; Eng. Pat. 132551, 1918) use 4 layers of platinum gauze, 0·0026 inch diameter wire and 80 mesh, in close contact. The catalyst is cylindrical, closed at the bottom with a silica plate, and hangs inside a chamber lined with glazed bricks. No preheating of the gas is used, the heat radiated from the gauze and walls of the chamber sufficing. The yield is said to be 90 to 91 p.c., and 70 lbs. of ammonia are oxidised per oz. of platinum in 24 hours. This apparatus does not appear to have been in use on the large scale.

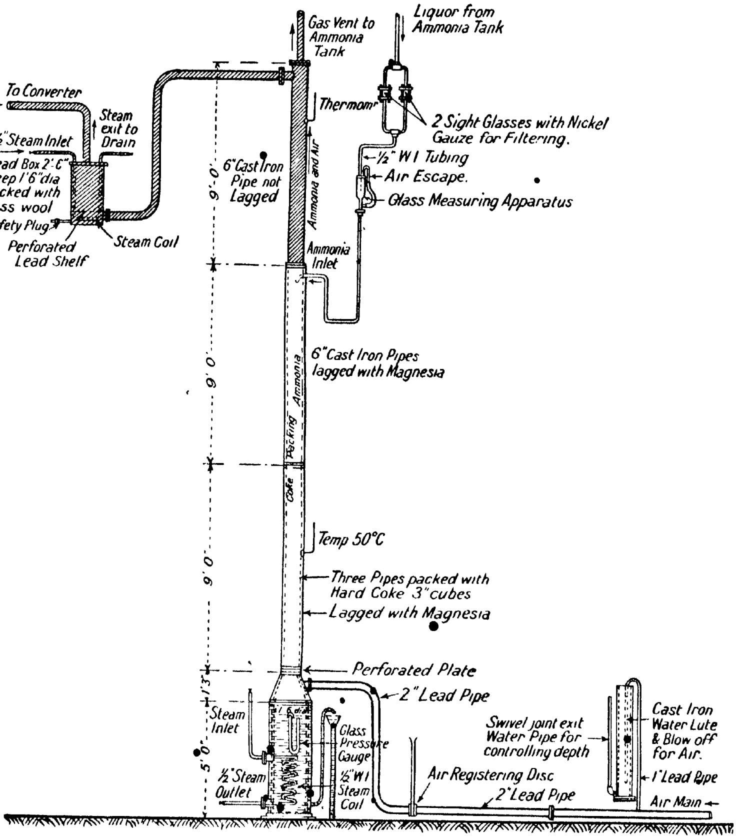

FIG. 12.

Apparatus for producing mixture of Ammonia and Air.

Perley (Chem. & Met. Eng. 1920, 22, 125; J. Ind. Eng. Chem. 1920, 12, 5, 119) describes a new form of interchanger. A cylindrical 4-layer gauze is used. The conversion efficiency is said to be 95 p.c.; 100 lbs. of ammonia are oxidised per 24 hours per oz. of platinum. The gases are preheated to 600°C. by mixing preheated air with ammonia gas in an iron pipe lined with silica. The same author states that very small amounts of phosphine are detrimental; this impurity, which may be present in cyanamide ammonia, may be removed (Parsons and Jones, Eng. Pat. 136342, 1920) by passing the mixture of ammonia and air, heated to 50°–60°C. over a catalyst composed of 'a metal of the silver group' on a support of carbonised cellulose fibre. Ammonium phosphate is formed, which is retained by the carbon. Taylor and Capps (J. Ind. Eng. Chem. 1918, 10, 457) state that acetylene present to the extent of 0·02 p.c. reduces the yield from 95 p.c. to 89 p.c., and 0·1 p.c. to 65 p.c. Later (*ibid.* 1919, 11, 27) they find that phosphine is very harmful; 2 to 3 parts per million reduce the yield several p.c. The effect of acetylene is probably due to phosphine as impurity. Decarrière (Compt. rend. 1921, 172, 1663; 173, 148; 1922, 174, 460, 756) finds that small amounts of hydrogen (0·44 p.c. by vol.) slightly increase the activity of the platinum catalyst, but larger amounts (1·0–1·5 p.c.) slightly reduce it. Hydrogen sulphide lowers the activity, the effect depending on the concentration rather than on the total amount which has passed over the catalyst. Acetylene causes, during the first few minutes, a slight rise in the yield, followed by a fall which is proportional to the absolute amount of impurity which has passed rather than to the concentration, and continues even when pure gases are then used. Hydrogen phosphide, even to the extent of 0·00002 p.c., reduces the yield 30 p.c., and with 0·02 p.c. the yield falls from 93·8 p.c. to 3·9 p.c. The activity is regenerated when the impurity is removed. The presence of H_2S counteracts the injurious effects of C_2H_2 and PH_3.

The ammonia oxidation plant of the Höchst Farbwerke (vormals Meister, Lucius und Bruning) (J. Soc. Chem. Ind., 1921, 40, 185 R) is situated at Höchst, on the right bank of the Main about 10 miles from Mainz. It is about 2 miles from the works of the Griesheim Elektron Co., with which, however, it has no connection. During the war an amalgamation with the Badische interests took place, synthetic ammonia from Oppau being supplied to Höchst for oxidation (*see* p. 571). There was before the war an oxidation plant at Hochst, comprising 37 converters fitted with circular platinum gauzes about 7·2 inches diameter, contained in vessels similar to those used for contact sulphuric acid. The efficiency of this plant, which produced about 54,000 tons of nitric acid per annum, was not above 80 p.c., and a new plant, completed in February 1919, was erected in its place at a cost of about £1,000,000. This plant has a capacity of 24,000 tons of ammonia, or 140,000 tons of nitric acid, per annum.

In addition to synthetic ammonia, arriving as 25-27 p.c. liquor from Oppau, gas liquor ammonia (20 p.c. NH_3), and cyanamide ammonia liquor (22-27 p.c.) from Knapsack (*see* p. 579) were received, the liquor being stored in 4 overhead spherical steel tanks, each of 264,200 gallons capacity. The liquor was rectified in 4 stills, 1 spare, of the Savalle type with 15 effects, each with a capacity of 20 tons of ammonia daily. The gas not used for oxidation was absorbed in a plate tower 30-40 feet high. Ammonia from gas liquor was scrubbed with caustic soda solution of 48°-53° Tw. and then passed through charcoal purifiers in the usual way to remove sulphur compounds. The ammonia gas from the stills was freed from moisture by refrigeration with ice-cold water; the presence of moisture caused scaling of the iron pipes and was also believed to be prejudicial to the conversion, although there is no evidence of this.

The ammonia gas and air were metered through Venturi meters and driven by ten 55 kw. centrifugal blowers to the filters and converters. The mixture contained 12·5 p.c. by volume of ammonia, regulated within narrow limits. The ammonia supply pipe was 6 inches diameter and the air pipe 18 inches diameter. The air was filtered through cloths in a wooden box and the mixed gas was carefully filtered from dust and ammonium salt fumes through 8 layers of linen cloth in chambers 9 feet by 5 feet.

The gas passed under 6 inches water pressure through two central mains in the converter house, from which it was diverted to the 224 converters, each provided with a circular platinum gauze catalyst of 20 inches diameter, or 2·12 square feet cross section. The maximum output of each converter was 1·5 tons of nitric acid per 24 hours, the efficiency of oxidation being 89 p.c. The efficiency from ammonia to dilute acid (including the efficiency of the absorption plant) was 87 p.c., that from ammonia to strong acid (including the concentrating plant) was 84 p.c. The body of the converter (Fig. 13) consists of cast iron, in four sections with flanges. The two middle sections were 18 inches and 12 inches high, and supported the catalyst between them; the conical top and bottom pieces were each 3 feet 6 inches high. The top cone was lined with sheet nickel to protect it from the hot gas. The catalyst, clamped between asbestos rings, was started by heating to redness by a hydrogen or coal-gas flame inserted below it through a lighting hole shown in the figure.

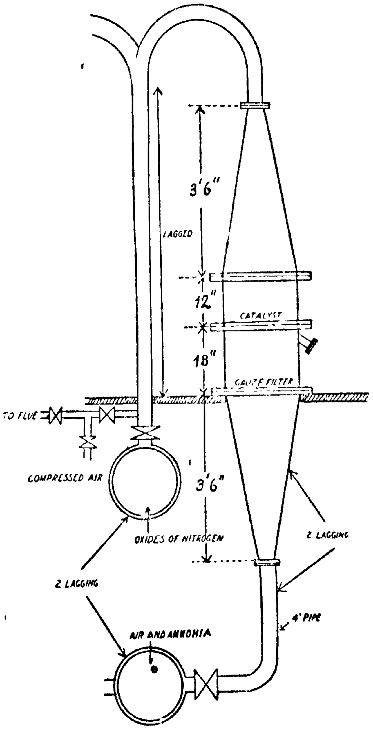

FIG. 13.

Ammonia Oxidation Converter at Höchst.

The exact construction of the catalyst has been differently stated. It has been asserted that it consists of 2, 3, or 4 platinum gauzes, 20 inches diameter, of 0·06 mm. wire with 80 meshes to the linear inch. The gauzes are possibly spot-welded, and are supported on a grid of 10 stout platinum wires, 1 mm. diameter, spaced at 10 cm. distance. The total weight of platinum in the catalyst has been stated as 333 grms,, which does not agree very well with the details of construction, but is probably approximately correct.

The converters were arranged in 2 sets of 7 or 8 on each side of separate inlet and outlet mains, the latter 1 foot in diameter and connected with the converters by 4-inch pipes, lagged with diatomite brick shaped to fit, cemented and wired. The upper bend pipe of the converter was not lagged, so as to allow for expansion. Before entering the converters the gas passed from a common main to a vertical, lagged, multitubular preheater, 15 feet by 5 feet external dimensions, in which it was heated by steam. The purpose of this was to prevent condensation of acid from the hot gases coming from the converter when these were passed through the heat exchanger which followed. In this, which was identical in dimensions with the preheater, the warmed gas passed in counter current to the gas from the converters, and left at 200°C. Two heaters so arranged served 14 converters. The temperature of the catalyst was about 800°; the gas left the converter at 650°–700°. In starting the converters extra air could be added and the only partly converted exit gas by-passed to a chimney until the gauze was activated. Gate valves were used, with a slight air pressure on the side of the valve not in contact with the gases, to prevent leakage. In 56 of the latest type of converters, the gas was passed by a lagged 3-feet main through 2 tubular boilers, leaving these at 270° to the heat exchanger. In this way 4 tons of water were evaporated per hour and the steam was used for warming the gas, as described above. From 1 to 3 men only are necessary to look after all the converters.

The gases containing nitric oxide and steam coming from the converters were passed through 8 cast-iron mains 18 inches diameter, supported on 3 ferro-concrete bridges, to 4 rows of 8 absorption towers. Each row of towers was provided with 12 intensive coolers of special design, *i.e.* 48 coolers in all. These coolers (Fig. 14) were of aluminium, with an annular space between the outer wall and an inner vessel, the gas entering above through 4 inlets. In them, on account of the rapidity with which the gas passed through, practically no acid was condensed, but only water. The condensate was put down the fifth absorption tower. The gas left the set of 4 coolers at 30°C. through 4 pottery mains 1 foot diameter, joining to a single brick chamber at the base of each set of 8 towers attached to 56 converters. Secondary air was admitted at this point (not before the coolers).

The towers are 41 feet high and 21 feet diameter, internally. The walls comprise 3 layers of brickwork, the outer layer of bricks 6 inches by 4 inches, set in a mixture of sodium silicate and kieselguhr. The top of the tower is slightly domed and there is a central partition in each tower, the gas passing up one side and down the other, and then going to the next tower through a brick channel at the base. The towers are packed with stoneware rings. The total internal volume of all the towers is 35,320 cu. feet, which amounts to only 81 cu. feet per lb. NO_2 absorbed per minute as compared with 350 cu. feet calculated by the formula proposed by J. R. Partington and L. H. Parker (p. 594), or 1500 cu. feet as used at the French works at Bassens. The reason why this small tower capacity is effective is clear when it is remembered that at Hochst no less than 25 p.c. of the oxides were absorbed as nitrate by saturated sodium carbonate solution fed to the last two towers. The liquor in the first of these towers is allowed to become acid, so that the nitrite is converted into nitrate, whilst that in the second is kept alkaline, to absorb the oxides of nitrogen driven out of the first when conversion into nitrate occurs (*see* p. 604; Eng. Pat. 129699, 1919, of Partington and Rideal). The solution of nitrate was evaporated by the waste heat of the converters. The remaining towers were fed with water for the production of nitric acid. The efficiency of absorption plant was 97 p.c. Each tower is stated to have cost 40,000 marks. Acid of 50 p.c. strength was obtained from the first tower of the series, the liquid being circulated in the towers by 8-inch chrome steel centrifugal pumps each fed by a 3–4-inch pottery main and delivering through a silicon-iron pipe of the same diameter to the top of the tower, two delivery pipes being used to each tower. The metal pipes were coned and fitted in the same way as the pottery pipes. Acid distribution was effected at the top of the tower by a revolving ribbed disc, turned by a gear shaft at 80 revs. per minute.

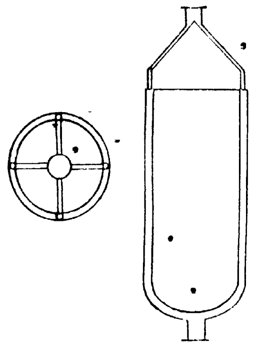
FIG. 14.

Aluminium Cooler.

The acid from the towers was passed to the coolers, consisting of S-pipes of silicon-iron cooled externally with water. There were also intercoolers between each pair of towers except the last, and the temperature was kept as low as possible, 25°C. in winter and 40°C. in summer. The fact that the dilute acid towers would probably work slightly better if warm (*see* Partington and Parker, *l.c.*) does not seem to have been appreciated. In summer iced water was used in the coolers. Large stoneware receivers were placed above the coolers to serve as acid reservoirs. The circulation in each tower was 110 gallons per minute; the loss of acid in the whole system did not exceed 2 p.c.

Twelve stock tanks of brickwork, each holding 1412 cu. feet, received the tower acid, from the receivers at the base of the towers, through tapered pottery pipes. No fan was used with the towers.

The tower acid was concentrated by mixing 1 part of 50 p.c. tower acid with 7 parts of sulphuric acid, in 5 mixing vessels with mechanical stirrers, and then denitrating. About 42,000 tons of sulphuric acid were used per month, but practically all was recovered. (In France, 2·5–3 parts of sulphuric acid only were used, but the nitric acid obtained was of 85 p.c. strength, as compared with a more concentrated acid obtained at Hochst.) The nitric acid was recovered partly in 2 rows of 9 silicon-iron towers, 4 feet diameter and 25 feet high, and partly in stone towers, with cast-iron pipe jackets, 35 feet high and 3 feet 6 inches external diameter, the walls being 9 inches thick. Steam at 150°C. was introduced at the base by a 1-inch lead pipe just above the exit for the denitrated acid. The nitric acid vapour from the top of the denitrator passed to a cooler of S-shaped silicon-iron pipes. The acid to be denitrated entered half-way down the cooler, and acid from stock was sent down the upper part to assist condensation. Oxides of nitrogen were removed from the nitric acid by a current of air and recovered in 20 absorption towers. The completely denitrated sulphuric acid was cooled in a water-cooled cast-iron cooler and collected in a large lead-lined tank of artificial stone. It contained about 70 p.c. sulphuric acid, and was reconcentrated in a Kessler apparatus or in Hoenig's modified Pauling apparatus (*see* Zeitsch. angew. Chem 1921, 34, 168, 173). The latter was said to be very efficient (In French practice, a denitrating column 20 feet high and 18 inches internal diameter produced 6–8 tons of nitric acid per day with an overall yield of 85–87 p.c. on the ammonia burnt in the Ostwald type catalysts. The consumption of fuel in reconcentrating the sulphuric acid was 15–20 p.c. of the weight of nitric acid produced.)

It is of interest to compare the mode of operation at Hochst, representing the latest German practice, with the indications obtained by experimental work carried out for the Munitions Inventions Department. The separation of water from the converter gas by rapid cooling was the subject of Eng. Pat. 131942, 1918. The object of this procedure, which is combined with the addition of secondary air *after* the coolers, is to keep the gas as concentrated as possible in the oxidation and absorption towers. It is clear from the equation $4NH_3+5O_2=4NO+6H_2O$ that the uncooled converter gas contains nitric oxide and steam in the ratio 2 to 3 by volume, so that if the steam is taken out a considerable concentration in oxides of nitrogen results. The fact that the condensate is afterwards put down a weak acid tower may have tended to obscure the rationale of the method. The use of alkali to finish the absorption was carried out in the manner specified in Eng. Pat. 129699, 1919; this effected a considerable economy of tower space. The use of sulphuric acid as an absorbent, which was tried at Leverkusen and found unsatisfactory, was also the subject of a long series of experiments, which showed that it was not an efficient method of absorption.

In the ammonia oxidation plant at Muscle Shoals (*see* p. 577) there are 6 converter houses and a meter room to each, the air being passed by blowers through a 5½-feet duct and mixed with ammonia gas by meters in the ratio of 1 vol. ammonia to 9 or 10 vols. air. The mixing is performed in 12 mild steel mixing tanks, 8 feet diameter and 30 feet high, packed with 6-inch spiral rings, from which the gas passes to the converters.

There are 4 rows of 29 converters in each converter house, or 696 in all, spaced 5 feet apart. The gas enters at the top through an iron pipe. The body of the converter is an aluminium box, rectangular in section, 14 inches by 28 inches and 5 feet high. At the base is a single horizontal sheet of platinum wire gauze, of 0·003-inch wire and 80 meshes to the linear inch, weighing 4·6 ozs. troy. Each gauze is heated by an 8 kw. transformer at 21 volts and 375 amps. to about 750°C. The converted gas passes down through an iron cone attached to the converter body and along an iron pipe to a concrete flue lined with acid-resisting tiles laid in acid-proof cement, leading to the coolers. Each converter produces 900 lbs. of nitric acid per 24 hours.

The high-temperature coolers consist of 24 horizontal steam boilers at 25 lbs. pressure. In passing through the tubes the temperature of the gas is reduced from 600°C. to 200°C. The gas then passes to low-temperature coolers, 12 of which are used, connected with the boilers by 30-inch aluminium pipes. Each low-temperature cooler is a rectangular brickwork chamber divided into 5 compartments by 4 walls which do not quite reach across, so that the gas is compelled to take a zig-zag course. Suspended from the roof of each compartment are 140 tubes, 5 inches diameter and 7 feet long, in 2 compartments of stoneware and in 3 of silicon-iron. Each tube has an outlet lip at the top and an internal tube through which water flows. The gas is cooled on the outer surfaces of these tubes to 30°C. and some nitric acid is condensed, which drains off to No. 3 well of the absorption system.

From the coolers the gas passes to 12 oxidation towers, 15 feet square, of chemical brickwork, each divided internally by 2 walls into 4 compartments. The gas passes up one compartment, over the top of the dividing wall, down the next compartment, up the next compartment, and down the last. The practically fully oxidised gas now passes to the absorption towers. All the towers are housed. There are 24 absorption towers, 35 feet square and 60 feet high, of brick, divided into 4 compartments as before. The first tower of each unit of two is half packed with 6-inch spiral rings and half with 3-inch spiral rings. The second tower is completely packed with 3-inch rings. Water is circulated in counter-current to the gas and 50 p.c. acid is recovered from the towers. The acid is pumped by air lifts, each single stage, throwing 50 gallons of acid per minute. One lift is provided for each compartment, or 96 in all with 24 spares (*see* J. Oliphant, Chem. & Met. Eng. 1920, 22, 408). To accommodate these lifts there are 120 iron wells, 12 inches diameter and 100 feet deep. The lifts consist of 3-inch aluminium pipe (which was not found satisfactory in England for nitric acid), with silicon-iron flanges. The towers also stand in aluminium saucers. Air at 100 lbs. pressure is supplied by a 1-inch pipe, and the acid in each well section is cooled by water flowing in the well. Leakage of acid is indicated by a signal lamp lighting up owing to increased conductivity. Between the two towers of each unit is an aluminium fan, and after the second tower a similar fan exhausts the residual gas to the free air. The compressed air from the lifts is also discharged into the free air, which must cause considerable loss of oxides of nitrogen and acid spray. The tower acid passes to 12 aluminium weighing tanks on scales, and is discharged to 12 storage tanks of acid brick and concrete, from which it is run off by a 3-inch aluminium siphon. When operating at full capacity the plant produces 280 tons of nitric acid per day.

A comparison of the sizes and outputs of various types of platinum gauze converters is given in the following table. These results were all obtained by J. R. Partington in long runs under various conditions, with converters of cross-section 4 inches by 6 inches, *i.e.* full-sized technical units. For comparison, the Ostwald type is given first.

Type of converter	Catalyst	Method of heating	Conversion efficiency	Output kgm. HNO_3 per grm Pt per 24 hours
Ostwald	Platinum foil	Regenerative	90–95 p.c.	1·7–2
Frank-Caro	Single platinum gauze	Electrical	90–93 ,,	11
Kaiser	4 superposed platinum gauzes	Preheating of gases	95 ,,	12
Partington	2 platinum gauzes slightly separated	Electrical or preheating of gases	95 ,,	16
Partington[1] with oxygen	2 platinum gauzes in contact	Gases+steam preheated to 500°–600°	98–99 ,,	21

Catalysts other than Platinum. In the preliminary account of the oxidation of ammonia the use of numerous catalysts other than platinum was described. A large number of these have been found unsuitable in practice for various reasons. In some cases the catalyst is not sufficiently active; in others it rapidly deteriorates in use; and finally, it may be necessary to use such a high temperature that difficulties are encountered in the construction of the containing vessel. The best non-platinum catalysts seem to be those having as a base oxide of iron or chromium (the latter prepared (Eng. Pat. 126716, 1917) by the gentle ignition of ammonium dichromate and afterwards compressed into pastilles), together with up to 10 p.c., or even more, of 'promoters,' especially oxides of cerium and bismuth (Eng. Pat. 126715, 1917). Catalysts of this type are described in the patents of Farbenfabrik vorm. F. Bayer (*see* above), and are used by the Badische Co. Plumbites and manganates, although fairly efficient catalysts, act too strongly on the containing vessels at the high temperatures required to be of much use. In all cases, a higher temperature, 800° as compared with 600°–700°, is required with oxide catalysts than with platinum, and the catalyst must be in thicker layers. The cheapness of the oxide catalysts, and the fact that they are less susceptible to poisons than platinum, are points in their favour.

The Bayer process is in use at the Leverkusen works of that firm, the plant being erected early in the war to replace Chile nitrate.

The ammonia came partly from synthetic sulphate and partly from gas liquor. The ammonium sulphate was dissolved on one side of the works in 12 dissolvers of 1000 gallons' capacity; and milk of lime was prepared in a parallel row of vats on the other side. Between were 2 rows of 10 ammonia stills in each, also of about 1000 gallons capacity, fitted with agitators and steam coils, and leading to a common main of 18 inches diameter. Gas liquor was distilled from milk of lime in vertical stills of 6 effects, the steam coils being in the bottom section. Four columns were installed. The ammonia gas was passed through a similar vertical column scrubber, in which it was washed with caustic soda solution. There were 2 scrubbers, 5 feet by 12 feet; the stills were 15 feet high and 4 feet diameter.

The ammonia gas was passed through a small balancing gasholder of 500 cubic feet capacity into a large holder of 1000 cu. m. capacity with an indicating dial. A mixture of air and ammonia containing 7–8 p.c. of ammonia was driven by separate centrifugal blowers to the converters, the air being filtered through cloth. Venturi meters controlled the mixture, which contained 7·5 p.c. by vol. of ammonia. The air passed through a cylindrical tubular heat exchanger (Eng. Pat. 145059, 1920), 12 feet by 12 feet, in counter current to the hot converter gas, leaving by an 18-inch pipe, a 6-inch by-pass being also provided. The ammonia was not preheated, but passed by a 4-inch pipe to a mixing chamber between the exchanger and converter. This mixing chamber in some cases consisted of an inclined cone 3 feet long and 4 feet diameter, the hot air entering the base and the ammonia and cold by-passed air tangentially. The mixture passed to the converter at 300°–360°.

The converters are sheet-iron cylinders lagged externally and lined with bricks, 15 feet high and 12 feet external diameter. They formerly had an axial tube 3 feet diameter, serving to convey cold air to equalise the temperature of the catalyst, but in the newer types, which have a diameter 1⅓ that of the older, this axial tube is omitted. The catalyst layer is deep, so that the time of contact is much longer than with platinum. There are first about 10 inches of fine granules resting on coarser granules on a perforated refractory plate. The gas passes upwards through the catalyst. The diameter of the catalyst granules varies from 5 to 10 mm. The diameter of the catalyst bed in the older type was 9 feet, the drop of pressure across it being about 10 cm. of water. The temperature of the catalyst is about 750°C. The average capacity of the older units was 4600 kg. ammonia per day; the new converters have a capacity of 15,000 kg. per day. The capacity of the whole plant is 6000–7000 tons of nitrate per month, with an overall efficiency of 80–85 p.c. The catalyst, provided by the Badische Co., consists of oxide of iron with promoters.

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[1] Results with converter 2 inches by 3 inches.

The absorption plant consists of three distinct units. These effect absorption in sodium carbonate, in water, and in sulphuric acid, respectively.

In the alkaline absorption section, each converter is connected with six towers, the first a small rectangular stone tower 12 feet high and 3 feet wide, acting mainly as a cooler. The second tower is cylindrical, 30 feet high and 8 feet diameter, of steel plates. The third tower is rectangular, of volvic stone, and 30 feet high, whilst the remaining three towers are like the second. There are 12 rows of these towers, the gases from which pass by a common main to a 60-feet tower 20 feet diameter, through which they are drawn by a fan. Saturated sodium carbonate solution is supplied to the tops of the first, second, sixth, and seventh towers, and drains to a granite tank, from which it is pumped to the top of the fourth tower, which is run slightly acid so as to cause conversion of all nitrite into nitrate. From this tower the sodium nitrate solution leaves by a 4-inch main.

In the water absorption section, erected in 1918, the gas from the converters is brought by a 3-feet main to 6 brick towers, 40 feet by 12 feet, arranged in 3 rows of 2 and packed with broken quartz. From these the gas passes through a rectangular brick flue, 6 feet by 3 feet, to 12 brick towers, 60 feet high and 13 feet internal diameter, the walls being 2 feet thick. After being drawn through these towers by a fan the gas is discharged to the free air through a 3-feet iron pipe. Water is fed to the last tower and circulated forward by centrifugal pumps. When the acid reaches the bottom of the fourth tower in the series of 12 it is cooled between successive towers and finally reaches a concentration of 40–50 p.c. nitric acid.

The latest plant is for absorption in sulphuric acid. There are 6 steel towers, 40 feet high and 8 feet diameter, the acid being cooled in coils between each pair of towers through which it is circulated. Nitric acid is recovered by distillation, although steam must be added. The results were not efficient on account of the difficulty of recovering nitric acid from the liquid after absorption.

Oxidation of Ammonia in Solution. Numerous experiments have been made on the oxidation of ammonia in solution (*a*) by catalysts, (*b*) by electrolysis. The results have not been promising. Herschkowitsch (Zeitsch. physikal. Chem. 1909, 65, 93) found that ammonia is oxidised by potassium permanganate in solution; the yield is influenced by concentration and is improved by the addition of ammonium salts. The action of persulphates has been investigated by Kempf (Ber. 1905, 3972) and by Levi and Migliorini (Gazz. chim. ital. 1908, 38, ii, 10). The product is mainly nitrogen. The catalytic autoxidation of ammonia by air was examined by N. Smith (Proc. Chem. Soc. 1906, 39); Loew (J. pr. Chem. 1878, 18, 298); M. Traube (Ges. Abh. 1881, 393); and M. Berthelot (Compt. rend. 1863, 56, 1170). Electrolytic oxidation has been studied by C. Frenzel (Zeitsch. anorg. Chem. 1902, 32, 319), F. Fichter and H. Kappeler (Zeitsch. Elektrochem. 1909, 15, 937; 1910, 16, 610; Chem. Zeit. 1912, 606). The use of copper salts in alkaline solution as catalysts in anodic oxidation has been studied by Traube and Biltz (Ber. 1906, 166) and Muller and Spitzer (*ibid.* 1905, 778). The primary product is nitrite; with copper as catalyst the formation of nitrate begins. The cost of electrical energy appears to be prohibitive.

Direct Production of Nitrates. J. R. Partington and E. K. Rideal (Eng. Pat. 129699, 1919) find that if gases containing oxides of nitrogen, such as are produced in arc furnaces or by the oxidation of ammonia, are passed through an alkaline solution, containing caustic soda, sodium carbonate, lime, or a suspension of calcium carbonate (limestone, or cyanamide sludge), all the nitrite in the mixture of nitrate and nitrite first produced is ultimately converted into nitrate.

During the first part of the absorption, a mixture of equimolecular amounts of nitrate and nitrite is formed:

$$1.\ 2Ca(OH)_2+4NO_2 \\ =Ca(NO_3)_2+Ca(NO_2)_2+2H_2O.$$

During this stage the reaction remains alkaline, and all the insoluble diluent gas associated with $4NO_2$ passes on through the apparatus.

When the reaction becomes neutral, the NO_2 begins to dissolve as a mixture of equimolecular amounts of nitrous and nitric acids:

$$2.\ 4NO_2+2H_2O=2HNO_3+2HNO_2.$$

The nitric acid at once decomposes the calcium nitrite in solution, and a mixture of equimolecular amounts of NO and NO_2, which may be written N_2O_3, is evolved:

$$3.\ Ca(NO_2)_2+2HNO_3=Ca(NO_3)_2+N_2O_3+H_2O.$$

At the same time the nitrous acid formed in reaction (2) undergoes decomposition, with evolution of N_2O_3:

$$4.\ 2HNO_2=N_2O_3+H_2O.$$

Thus, in the volume of indifferent gas which contained $4NO_2$ on entering the apparatus we have, when it leaves the apparatus, $2N_2O_3$, equivalent to the original concentration. This gas is now passed through empty towers, where the NO undergoes oxidation to NO_2 in presence of the excess of oxygen in the gas. The fully oxidised gas then passes to a second set of absorbers, where reaction (1) occurs.

The final solution contains only calcium nitrate, with a little free nitrous acid, which is removed by passing air through it. This air is then passed through the absorbers containing fresh milk of lime, to recover the oxides of nitrogen. The process may be used with gas containing as little as 1 p.c. by volume of NO_2, and at the ordinary temperature or with the solutions at 30°. The milk of lime may be used of such a strength as to give a resulting solution containing 50 p.c. $Ca(NO_3)_2$.

J. R. Partington, G. J. Jones, and T. K. Brownson (Eng. Pats. 134562, 136190, 1919) also find that, when a mixture of air, oxides of nitrogen, and a regulated amount of moisture (*e.g.* suitably treated gas from the oxidation of ammonia) is passed through a chamber, and jets of ammonia gas introduced, there is an instant separation of dry, solid, ammonium nitrate, perfectly free from nitrite. This settles out as a loose powder, which on standing for a few hours shrinks to a denser powder without caking. This product is less deliquescent than ordinary ammonium nitrate, and the process gives very satisfactory yields. The mechanism of the reaction is not yet quite clear, the net result appears to be:

$$2NO_2+2NH_3+H_2O+O=2NH_4NO_3.$$

If oxides of nitrogen and ammonia gas are mixed without the special precautions mentioned, considerable decomposition and loss occurs. The same experimenters also find that the fume of ammonium nitrate produced when *moist* oxides of nitrogen and ammonia are brought together, which, unlike that formed in the above process, does not readily condense, may be brought into the solid form by passing the fume through concentrated sulphuric acid. Very little absorption of ammonium nitrate by the liquid takes place, but the dried fume at once deposits solid ammonium nitrate on issuing from the acid.

A novel method of concentrating nitric acid is described in the patents of Meister, Lucius, and Brüning (Eng. Pats. 15948, 1911, and 4345, 1915). Acid of 60–62 p.c. is enriched with nitrogen peroxide, NO_2, which readily dissolves in it, and the liquid is subjected in a finely divided condition to the action of oxygen: $2NO_2+H_2O+O=2HNO_3$. The unchanged nitrogen peroxide is expelled by the current of oxygen, and the resulting concentrated acid is practically free from nitrous acid. In another process, aqueous nitric acid is agitated with excess of liquid nitrogen peroxide. Two layers are rapidly formed, each consisting of nitric acid holding nitrogen peroxide in solution. The upper layer consists of liquid nitrogen peroxide containing very concentrated nitric acid (98–99 p.c.) in solution, whilst the lower layer is a solution of nitrogen peroxide in weaker (75 p.c.) nitric acid. The upper layer may be separated and the nitrogen peroxide removed by distillation, when very concentrated nitric acid remains. The NO_2 removed is used again. These processes have been verified by J. R. Partington, who finds in addition that, if nitrogen peroxide and oxygen are passed through water for a sufficient length of time, the same two layers are formed. The importance of these reactions in cases where gases fairly rich in nitrogen peroxide, *e.g.* those from the oxidation of ammonia, are available, is evident.

The Häusser Process. Numerous processes, in which the union of oxygen and nitrogen of air is to be induced by the rise of temperature caused by the combustion of fuels, have been proposed (*cf.* Haber and Koenig, Zeitsch. Elektrochem. 1910, 16, 18; Norton, The Utilisation of Atmospheric Nitrogen). Although, as has been stated, no nitric acid is formed by the explosion of hydrogen and air, some is produced in the hotter flame obtained by enriching the air with oxygen. Acid is also formed by burning carbon monoxide in air under pressure. The amounts formed are small, and are mixed with large volumes of the products of combustion, so that *a priori* very little hope of successful methods appears in this quarter. Attention may, however, be directed to the process devised by Hausser (Chem. Trade J. 1914, 55, 46, 69), which seems promising. In this a mixture of air and a combustible gas, such as coal gas or coke-oven gas, is exploded in a gas-engine cylinder or bomb under pressure. The resulting gas contains only 0·3–0·6 p.c. nitric oxide by volume, so that an extensive absorption system would be necessary. Trials of the process were made on a small scale at Nuremberg and at Heeringen (Westphalia), which pointed to a yield of 135 grms. HNO_3 per cu. m. of fuel gas of calorific value 483 B.Th.U. per cu. foot, operating with an initial compression of 3·2 atm., with a pre-heat of 240°. It is claimed that an oil-spray, such as is used in Diesel engines, may also be applied. It is not difficult to see from the law of mass action that the best result should be obtained with an optimum proportion of air and fuel gas, the precise mixture depending on the composition of the fuel gas. Enriching the mixture with oxygen should also increase the yield. In any case, the proportion of nitric oxide in the exploded gas cannot exceed 1 p.c. by volume. A very careful discussion of the Hausser process will be found in the Nitrogen Products Committee's Report, 277–285; *see also* H. Noh (D. R. P. 306451, 1916); H. Woll (D. R. P. 316677, 1919); J. Görlinger, (D. R. P. 316253, 1919); Häusser (Stahl und Eisen, 1921, 41, 956, 999; J. Soc. Chem. Ind. 1922, 41, 253 R).

J. R. P.

2-**NITROBENZENE**-1 : 4-**DISULPHONIC ACID** is obtained as the sodium salt by acting on a boiling aqueous solution of sodium 4-chloro-3-nitrobenzene sulphonate with sodium sulphite.

NITROBENZENES *v.* BENZENE AND ITS HOMOLOGUES.

m-**NITROBENZENESULPHONIC ACID** is prepared by the action of fuming sulphuric acid upon nitrobenzene (Schmidt. Annalen, 120, 163), or by the action of chlorosulphonic acid on nitrobenzene dissolved in carbon disulphide. Deliquescent plates.

NITROGLYCERIN *v.* EXPLOSIVES.

NITROHYDROCHLORIC ACID *v.* AQUA REGIA.

NITROMAGNESITE. A mineral consisting of hydrated magnesium nitrate

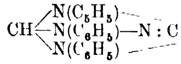
$$Mg(NO_3)_2+nH_2O$$

probably identical with the artificial monoclinic salt, $Mg(NO_3)_2,6H_2O$. It occurs as an efflorescence in limestone caves in association with nitrocalcite, and has been recorded with epsomite on marl in the Jura. L. S. J.

NITROMAGNITE or **DYNAMAGNITE** *v.* Explosives.

NITROMETER *v.* Analysis.

NITRON-1.4-Diphenyl-3.5-enolanilodihydrotriazole



$$CH\begin{cases}N(C_6H_5)\text{---}\\N(C_6H_5)\text{—}N:C\\N(C_6H_5)\text{---}\end{cases}$$

This compound, discovered by Busch (Ber. 1905, 38, 856), forms a nitrate almost insoluble in water and is well suited for the detection and estimation of nitric acid. The reagent can be prepared in the following way: Twenty grams of thiocarbanilide are heated with 0·5 litre of dry benzene under a reflux condenser, and dry mercuric or lead oxide is added in small portions, so long as a black precipitate is formed. The metallic sulphide is filtered off, the hot solution treated with the calculated quantity (10 grms.) of phenylhydrazine and concentrated to 50 c.c. On cooling, if necessary with addition of some petroleum spirit, the liquid solidifies to a crystalline mass of triphenylamino-guanidine. This is drained, washed with ether, dried, and heated for two hours in a sealed tube at 175° with twice its weight of 90 p.c. formic acid. The product is treated with 10 times its volume of water, filtered and the base precipitated by ammonia and extracted with chloroform. The chloroform solution is dried with potassium carbonate, concentrated to one-fourth, and, after addition of a few drops of light petroleum, allowed to crystallise.

Detection of nitric acid, free and combined.—Five c.c. of the solution under examination are mixed with 1 drop of dilute sulphuric acid and 5-6 drops of a 10 p.c. solution of nitron in 5 p.c. acetic acid are added. If nitric acid be present, a voluminous white precipitate is produced, or, if the quantity be very small, fine needles separate after some time. One part of nitric acid in 60,000 can be detected at the ordinary temperature, and 1 in 80,000 at 0°. Some other acids also give precipitates, but these can in most cases be easily removed before making the test, namely, hydrobromic acid by means of chlorine, hydriodic acid by oxidation with iodate and separation of the iodine, and nitrous and chromic acids by treatment with hydrazine sulphate. Chloric (1 : 4000), perchloric (1 : 50,000), thiocyanic (1 : 51,000), ferrocyanic, ferricyanic, and picric acids also interfere.

Determination of nitric acid.—The substance (containing about 0·1 gram of nitric acid) is dissolved in 80–100 c.c. of water, 10 drops of dilute sulphuric acid are added, the liquid is heated nearly to boiling and treated with 10 12 c.c. of the solution of nitron in acetic acid. The mixture is allowed to stand 1½–2 hours in ice-water, the precipitate collected, washed with the filtrate and then with 10–12 c.c. of ice-water in small portions. The precipitate is dried at 110° and weighed, the weight multiplied by 0·169 gives the amount of nitric acid. The nitron may be regenerated from the precipitate by shaking with ammonia and extracting with chloroform (*see also* Busch, Zeitsch. Nahr. Genussm. 1905, 9, 464).

Detection and determination of nitrate in presence of nitrite.—The substance is dissolved in a small quantity of water, and the solution allowed to drop gradually on to finely-powdered hydrazine sulphate contained in a beaker cooled externally with water. When the evolution of nitrogen, due to the decomposition of nitrite, has ceased, the solution is made up to 100 c.c. and treated with nitron as above described.

Gutbier (Zeitsch. angew. Chem. 1905, 18, 497), who critically examined the method, and modified it slightly, finds that there is a loss of 0·1–0·25 p.c., due to the solubility of nitron nitrate in water, otherwise it gives very good results, not only with potassium nitrate alone, but also with mixtures of the nitrate with potassium permanganate and bichromate, calcium and magnesium sulphates, potassium and sodium chlorides, alum and potassium bichromate, calcium carbonate and potassium bromide. If iodides be present, they must be destroyed by the cautious addition to the boiling solution of potassium iodate and acetic acid, till all the iodine is boiled off.

For the determination of *nitric acid in presence of nitrous acid*, the latter is determined in a portion of the solution by titration with permanganate. In another portion the nitrous acid is oxidised by hydrogen peroxide and the total nitric acid determined as nitron nitrate (Busch, Ber. 1906, 39, 1401).

According to Litzendorff (Zeitsch. angew. Chem. 1907, 20, 2209) the nitron method lends itself very well to the determination of nitric acid in soils which contain at least 2–3 mgs. of nitrogen (as nitrate) per 100 grms. In the case of poorer soils, or of extracts sterilised by heat, the evaporated extracts tend to contain some substance which inhibits the crystallisation of nitron nitrate. This substance may be destroyed by the use of hydrogen peroxide.

Busch and Schneider (Zeitsch. ges. Schiess- und Sprengstoffwesen, 1, 232) have applied the method to the determination of the nitric acid radicle in cellulose nitrates and to the analysis of nitrating acid mixtures and waste acids. To 0·2 grm. of cellulose nitrate are added 5 c.c. of 30 p.c. sodium hydroxide solution and 10 c.c. of 3 p.c. hydrogen peroxide. The mixture is heated for some minutes on the water-bath until solution is complete; 40 c.c. of water and 10 c.c. of hydrogen peroxide are then added, and the liquid is heated to 50°. After adding 40 c.c. of 5 p.c. sulphuric acid and heating to 80°, 12 c.c. of a 10 p.c. solution of nitron in 5 p.c. acetic acid are added. The mixture is cooled for 1–2 hours in ice-water and the precipitate collected and washed, as above described, and weighed as $C_{20}H_{16}M_4,HNO_3$ and the percentage of nitrogen calculated, using 0·0373 as factor.

Hes (Zeitsch. anal. Chem. 1909, 48, 81) finds that dextrin, gelatin, and probably other organic compounds hinder the crystallisation of the nitron nitrate, but the presence of aluminium sulphate, magnesium sulphate, ammonium sulphate, potassium phosphate, magnesium chloride, tartaric acid, citric acid, sucrose, and dextrose does not affect the accuracy of the method, provided the precipitate is sufficiently washed; oxalic acid causes high results. Chloric acid precipitates nitron quantitatively as the chlorate if the solution contains about 0·25 p.c.

of chloric acid, and nitric and chloric acids may be determined in the presence of each other if the quantity of one be known.

Franzen and Löhmann (J. pr. Chem. 1909, 79, 330) find that nitric acid can be accurately determined by means of nitron in solutions containing large quantities of organic matter, provided 2–2·5 c.c. of concentrated sulphuric acid be added for each 200 c.c. of solution. This addition of sulphuric acid prevents any co-precipitation of nitron oxalate and also the formation of a colloidal solution of nitron nitrate.

Paal and Ganghofer (Zeitsch. anal. Chem. 1909, 48, 545) on repeating the work of Hes found that dextrin only delayed the separation of the nitron precipitate, 16 hours instead of 4 being needed for the purpose, otherwise it was without sensible influence on the accuracy of the results. Peptone might be removed by normal lead acetate, formaldehyde, or by tannin and lead acetate, with the addition of 20–25 drops of sulphuric acid, when accurate results were obtained. Small quantities of gelatin, beyond retarding the formation of the precipitate, exercised no disturbing influence; larger quantities should be removed by tannin and lead acetate. Saltpetre in meat and meat extracts can be conveniently determined by means of nitron.

Cope and Barab (J. Amer. Chem. Soc. 1917, 39, 504) find that the nitron method yields good results with *nitromannite* and *nitrostarch*. With *nitroglycerin* satisfactory analyses may be made as follows: The nitroglycerin is weighed out in a 100 c.c. conical flask to which an air condenser, 25 cm. long, is attached by means of a ground joint. About 5 c.c. of 30 p.c. sodium hydroxide and 5 c.c. of 3 p.c. hydrogen peroxide are added, and then about 15 drops of 30 p.c. hydrogen peroxide. The mixture is heated on the water-bath for ten minutes, by which time the gas evolution has moderated considerably, and then 10–15 drops of 30 p.c. peroxide are again added. This operation is repeated over a period of two hours, and twice at half-hour intervals. The condenser is removed, 10–15 drops of 30 p.c. hydrogen peroxide are added, a splash head is attached to the flask by means of a rubber stopper, and the flask heated for a few minutes over a free flame. The addition of hydrogen peroxide and the heating are repeated twice and the solution is finally boiled down to a volume of about 3 c.c. Water (40 c.c.) and 10 c.c. of 3 p.c. hydrogen peroxide are added, the liquid heated to 50°, acidified with 40 c.c. of 5 p.c. sulphuric acid, and 12 c.c. of 10 p.c. nitron solution added.

Trinitrocresol and *dinitrophenol* can be directly precipitated with nitron, the addition compound of trinitrocresol with nitron being the most insoluble known compound of trinitrocresol, as nitron picrate is the most insoluble known compound of picric acid (Analyst, 1917, 216).

Perchloric acid can be determined in the same way as nitric acid. Minute quantities of *oxides of nitrogen in air* can be determined by shaking several litres of the air with 10 c.c. each of 5 p.c. potassium hydroxide and 3 p.c. hydrogen peroxide solutions and precipitating the nitric acid in the usual way, avoiding unnecessary dilution.

Solutions of nitron are not very stable and are best prepared in small quantities as required, by dissolving 1 gram of the reagent in 10 c.c. of 5 p.c. acetic acid and filtering through an alundum crucible into a dark bottle. The reagent can be recovered from filtrates by precipitating with a slight excess of ammonia, and from precipitates by warming with dilute ammonia to 60°, filtering quickly and washing the nitron with cold water, then digesting with 5 p.c. acetic acid to dissolve it and finally reprecipitating with ammonia and washing. Decomposition may be avoided by conducting the filtering and washing in an inert atmosphere and as much as possible away from light (J. Soc. Chem. Ind. 1917, 473).

NITRONES. Compounds comparable in structure with the tautomeric forms of oximes and with ketene. The simple nitrones are produced by the alkylation of oximes, or by the action of aldehydes on N-substituted hydroxylamines. Often formulated as cyclic ethers. The 'keto'-nitrones are obtained by the action of aliphatic diazo- compounds on nitroso- compounds.

NITROPHENINE YELLOW *v.* PRIMULINE AND ITS DERIVATIVES.

NITROPHENOLS AND THEIR HOMOLOGUES. Phenol may be nitrated very readily, and to produce the mono-nitro derivatives it is sufficient to treat it with dilute nitric acid in the cold. The *ortho-* and *para*-nitrophenols, together with some tarry matter, are thus formed. The *ortho-* compound is separated by steam distillation, whilst the non-volatile *para-* compound is purified by repeated crystallisations from xylene (Hofmann, Annalen, 1857, 103, 347; Fritsche, *ibid.* 1859, 110, 150; Schall, Ber. 1883, 16, 1901; Neumann, *ibid.* 1885, 18, 3320).

If the nitric acid is vigorously stirred, during and for about half an hour after the addition to it of the phenol, an 18 p.c. yield of *p*-nitrophenol is obtained without any formation of tar. The best yield is obtained at 25°. Below 4° nitration cannot be effected (Hart, J. Amer. Chem. Soc. 1910, 32, 1105; *v.* Pictet, J. Soc. Chem. Ind. 1911, 683).

Phenol may be first condensed with an aromatic sulphonic chloride in presence of an alkali, the ester so formed, on nitration, yields, without formation of tarry products, a dinitro-derivative, which on hydrolysis with an aqueous solution of a caustic alkali, yields the alkali salt of *p*-nitrophenol, together with that of *o*-nitrotoluene-*p*-sulphonic acid (Eng. Pat. 24193, 1895; J. Soc. Chem. Ind. 1897). Nitration of phenyl phosphate $(\mathrm{POCOC_6H_5})_3$ gives tri-*p*-nitrophenol which by hydrolysis yields pure *p*-nitrophenol. *o*-Nitro-phenol, almost free from the *p*-isomeride, may be obtained by converting phenol into the *p*-sulphonate, then nitrating it with sodium nitrate and sulphuric acid; on hydrolysis the $\mathrm{HSO_3}$ group is removed (Paul, *ibid.* 1897, 62); or by treating nitro-benzene with potash (Wohl, Ber. 1899, 32, 3486). *o-* and *p*-nitrophenols may also be obtained by the action of alkali hydroxides on the corresponding chlornitrobenzenes.

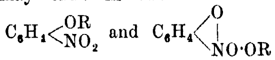
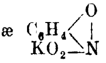
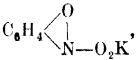
m-Nitrophenol is not formed by the direct nitration of phenol, but it may be prepared by boiling diazotised *m*-nitraniline with water

(Bantlin, *ibid.* 1878, 11, 2100; Henrique, Annalen, 1882, 215, 323).

The polynitrophenols are obtained by nitrating phenol with concentrated nitric acid, usually in the presence of sulphuric acid; by nitrating the lower nitro- compounds or their sulphonates; by treating the hydrocarbon with nitric acid in presence of mercury or mercury compounds, in which case the nitro and hydroxyl groups are introduced simultaneously into the benzene nucleus (Eng. Pat. 17521; D. R. P. 214045; J. Soc. Chem. Ind. 1907 1194; *ibid.* 1909, 1167; Chem. Zentr. 1908, i. 1005); and by other methods (Wender, Gazz. chim. ital. 1889, 19, 222; Oliveri-Tortorici, *ibid.* 1898, 28, 306; Reverdin and de la Harpe, Chem. Zeit. 1891, 16, 45; Frankland and Farmer. Chem. Soc. Trans. 1901, 1356; Robertson, *ibid.* 1902, 1475; Lobry de Bruyn, Rec. trav. chim. 13, 153; Pinnow and Koch, Ber. 1897, 30, 2857; Reverdin and Bucky, *ibid.* 1906, 39, 2679; Matuschek, Chem. Zeit. 1905, 29, 115; D. R. P. 91314; Frdl. iv. 40).

The nitrophenols are colourless or yellow crystalline substances. They are more acidic than the phenols, and they decompose alkaline carbonates. The nitrophenols may be reduced very readily to the corresponding amines, some of which are themselves valuable dyes, or are readily condensed with suitable aromatic compounds to form dyestuffs. By partial reduction nitroamines may be obtained (Hofer and Jakob, Ber. 1908, 41, 3187). The use of nitrophenols as precipitants for alkaloids is discussed by Rosenthaler and Gorner (Zeitsch. anal. Chem. 1910, 49, 340). The constitution of the nitrophenols has given rise to an important series of investigations by Hantzsch and others (Ber. 1902, 35, 1001, 1005; *ibid.* 1906, 39, 1073; *ibid.* 1907, 40, 330, 1556; Zeitsch. physikal. Chem. 1908, 61, 227; *see* also Rabe, *ibid.* 1901, 38, 175; Witt, Ber. 1876, 9, 522; Korczynski, *ibid.* 1909, 42, 167; Chem. Zentr. 1910, ii. 384; Scharwin, J. Russ. Phys. Chem. Soc. 1910, 42, 237; Seyewetz and Poizat, Compt. rend. 1909, 148, 1110; Baly, Edwards and Stewart, Chem. Soc. Trans. 1906, 514).

Whilst themselves colourless, or only faintly coloured, they give rise to two series of highly-coloured alkali salts—yellow and red, and on this account they were regarded as pseudo-acids. This view has been confirmed by the preparation of two series of ethers. The colourless phenol ethers are obtained under ordinary conditions of alkylation, and have the formula $NO_2{\cdot}C_6H_4OR$. The isomeric red ethers are much more difficult to prepare, owing, it is supposed, to their instability and to the ease with which they change into their colourless isomerides. The red ethers are formed by the action of alkyl iodide on the silver salts of the nitrophenols. The materials must, however, be absolutely pure and dry, and the reaction commenced at 0° and then raised to ordinary temperature. The red ethers, which have not been obtained quite pure, melt at least 20° below the colourless ethers; they are much more soluble in all solvents, giving coloured solutions, and on standing alone, and more readily in solvents or in the presence of hydrochloric acid, change into the colourless isomerides. The smallest trace of water hydrolyses them, forming the free nitrophenol, and this explains why, when a silver salt of a nitrophenol is alkylated without special precautions, free nitrophenol is often produced.

To explain the formation of the coloured salts and ether, it is supposed that nitrophenols and their derivatives, and also their homologues, may exist in two tautomeric modifications  $C_6H_4{<}^{OR}_{NO_2}$ and $C_6H_4{<}\begin{matrix}O\\|\\NO{\cdot}OR\end{matrix}$ (where R=H, a metal, or an alkyl radicle), of which the first is colourless, the second coloured; thus the constitution of the free colourless nitrophenols corresponds to the first formula, whilst the coloured nitrophenols, being much paler than their salts, correspond partly to the first, partly to the second formula. The coloured ethers correspond to the second formula, whilst the metallic salts, forming two series of coloured salts, have the two formulæ  $C_6H_4{<}\begin{matrix}O\\|\\KO_2{-}N\end{matrix}$ and  $C_6H_4{<}\begin{matrix}O\\|\\N{-}O_2K\end{matrix}$, of which the latter probably corresponds with the red salts, the former with the yellow salts. The orange salts sometimes obtained are probably solid solutions of the yellow and red salts (Hantzsch, Ber. 1907, 40, 330).

o-**Nitrophenol** $C_6H_4(NO_2)OH$ forms pale yellow needles or prisms, m.p. 44°, b.p. 214°, sp.gr. 1·447 (Schroder, Ber. 1879, 12, 563; Merz and Ris, *ibid.* 1886, 19, 1749). It has an aromatic smell, is sparingly soluble in cold water, more readily so in hot water, also in alcohol or ether. It behaves as a much stronger acid than the *p*- and *m*-isomerides.

m-**Nitrophenol** forms thick yellow crystals, m.p. 96°, b.p. 194°/70 mm. (Bantlin, *l.c.*); m.p. 93°, sp.gr. 1·827 at 19° (Fels, Zeitsch. Krystalographie, 1900, 32, 374). It is non-volatile in steam, and it is readily oxidised by Caro's reagent on warming, yielding 3- and 4-nitro-catechols, a part of it, however, being decomposed (Bamberger and Czerkis, J. pr. Chem. 1903, [ii.] 68, 480).

p-**Nitrophenol** forms colourless needles, m.p. 114°. It is non-volatile in steam, yields *p*-aminophenol when boiled with zinc-dust and water or when treated with hydrogen in presence of finely divided nickel, and when electrolysed in sulphuric acid forms *p*-aminophenolsulphonic acid. It reacts with alkali sulphide in presence of a copper salt, forming a green dyestuff (D.R.P. 101577; Chem. Zentr. 1899, i. 1091). *p*-Nitrophenol has been proposed for use as an indicator instead of methyl orange (Spiegel, Zeitsch. angew. Chem. 1904, 17, 715; J. Soc. Chem. Ind. 1904, 182; Goldberg and Naumann, *ibid.* 1903, 928). When heated with aqueous ammonia under pressure both the *o*- and the *p*-isomerides yield the corresponding nitranilines (Merz and Ris, *l.c.*). By mixing any of the mononitrophenols with quinine in presence of water, compounds are said to be obtained which are almost insoluble in water or dilute acid, and which may be used as internal antiseptics (U.S. Pat. 1005137, 1911; J. Soc. Chem Ind. 1911, 1333).

The nitrophenols may be sulphonated by treating them with fuming sulphuric acid, or in the case of the *ortho*- compound by chlorosulphonic acid. Mercury accelerates the reaction

(Post, Annalen, 1880, 205, 38; Nietzki and Lerch, Ber. 1889, 21, 3221; Gnehm and Knecht, J. pr. Chem. 1906, [ii.] 73, 519; *ibid.* 74, 92).

The sulphonic derivatives may also be formed by nitrating the required phenolsulphonic acid (Post and Stuckenberger, Annalen, 1880, 205, 45; Post, Ber. 1874, 7, 1233; D. R. P. 27271; Frdl. i. 324; J. Soc. Chem. Ind. 1885, 203; *see* also D. R. P. 114529; Chem. Zentr. 1900, ii. 1000).

Like phenol itself, the mono- as well as the polynitro- compounds form a number of metallic salts, ethers, and other compounds.

2 : 3-**Dinitrophenol** (Bantlin, *l.c.*) has m.p. 144°.

2 : 4-**Dinitrophenol** forms rhombic prisms, m.p. 114°–115° (Gauhe, Annalen, 1868, 147, 67; Pinnow, *l.c.*; Marqueyrol and Loriette, Bull. Soc. chim. 1919, [iv.] 25, 373); Sidgwick and Aldous, Chem. Soc. Trans. 1921, 1001. Warmed with sulphur and sodium sulphide it gives a black dye for cotton (D. R. P. 98437; Chem. Zentr. 1898, ii. 912). Ostromisslensky has prepared another 2 : 4-**dinitrophenol**, m.p. 85·1° (J. Russ. Phys. Chem. Soc. 1906, 38, 1351). The following methods have also been proposed for the preparation of 2 : 4-dinitrophenol. Vidal (Fr. Pat. 315696, 1902) dissolves 93 kilos. of phenol in 192 kilos. sulphuric acid (66°Bé.), and runs the solution into 162 kilos. of sodium nitrate dissolved in 1700 litres water. The mixture is allowed to remain for several hours and then slowly heated until effervescence ceases. The dinitro compound separates on cooling.

Wolffenstein and Boters (D. R. P. 214045, 1907) use the following method: 120 grams of benzene are mixed with 20 grams of mercury, and the mixture then treated with 270 grams of nitrogen tetroxide (either gaseous or liquefied) and allowed to stand for some days at ordinary temperature, when it solidifies to almost pure 2 : 4-dinitrophenol.

The usual method of preparation, however, is to decompose chlordinitrobenzene with hot aqueous sodium carbonate or hydroxide solution, precipitating the dinitrophenol by acidification after the reaction is completed.

2 : 5-**Dinitrophenol**, yellow needles, m.p. 108°, volatile in steam (Reverdin and Bucky, *l.c.*); m.p. 104° (Bantlin).

2 : 6-**Dinitrophenol**, light yellow, fine needles, m.p. 63°–64° (Hübner, Babcock and Schaumann, Ber. 1879, 12, 1346); 62·2° (Sidgwick and Aldous, *l.c.*).

3 : 4-**Dinitrophenol**, long silky colourless needles, m.p. 134° (Bantlin, *l.c.*).

3 : 5-**Dinitrophenol**, m.p. 122° (Lobry de Bruyn, *l.c.*; Heller, Ber. 1909, 42, 2191); 124° Holleman; 126·1°, Sidgwick and Taylor (Chem. Soc. Trans. 1922, 1853), who have determined its solubility in water and in benzene and its volatility in steam.

2 : 4 : 6-**Trinitrophenol**, *v.* Prussic acid.

2 : 4 : 5-(*β*-)**Trinitrophenol**, glistening needles, m.p. 96° (Henrique, *l.c.*).

2 : 3 : 6-(*γ*-)**Trinitrophenol**, small needles, m.p. 117°–118° (Henrique, *l.c.*).

2 : 3 : 5-**Trinitrophenol** is obtained by boiling diazotised trinitroaminophenol with absolute alcohol until nitrogen ceases to be evolved. It forms yellow needles, m.p. 119°–120°, and becomes ochreous and opaque when dried at 100°. It dyes silk and wool with a more orange shade than picric acid (Meldola and Hay, Chem. Soc. Trans. 1909, 1382).

2 : 3 : 4 : 6-**Tetranitrophenol**, golden-yellow needles, m.p. 130°, sometimes with explosion (Nietzki and Blumenthal, Ber. 1897, 30, 184); m.p. 140° (Blanksma, Rec. trav. chim. 1902, 21, 254). It dyes wool and silk an intense red-yellow colour. When boiled with water it forms trinitroresorcinol.

2 : 3 : 5 : 6-**Tetranitrophenol** is known in the form of its ethyl ether, m.p. 115° (Blanksma, *ibid.* 1905, 24, 40).

Pentanitrophenol $C_6(NO_2)_5OH$, m.p. 190°, when boiled with water is transformed into trinitrophloroglucin (Blanksma, *ibid.* 1902, 21, 254).

The polynitrophenols, when treated with potassium cyanide, yield the corresponding purpuric acids (Borsche and Böcker, Ber. 1903, 36, 4357; *ibid.* 1904, 37, 1843, 4388).

Nitraminophenols may be obtained by nitrating acetaminophenols, or, better, acetaminophenol acetate or similar compounds, then eliminating the acetyl group by hydrolysis (Reverdin and Dresel, *ibid.* 1904, 37, 4452), and also by other methods.

4-**Nitro**-2-**aminophenol** is obtained by the action of ammonium sulphide on 2 : 4-dinitrophenol. Crystallises with 1 mol. H_2O, m.p. 80°–90°, the anhydrous salt has m.p. 142°–143° (Post and Stuckenberg, *l.c.*; Kehrmann and Gauhe, Ber. 1897, 30, 2132).

5-**Nitro**-2-**aminophenol** may be prepared by nitrating the ethenyl derivative of *o*-aminophenol in the cold with a mixture of equal parts of nitric (40°Bé.) and sulphuric (monohydrate) acids; the product is then decomposed with concentrated hydrochloric acid. It forms yellow needles, m.p. 201°–202°. It yields fast bluish- and greenish-black azo dyes for wool (Eng. Pats. 7910, 7910A, 1905; D. R. P. 165650; J. Soc. Chem. Ind. 1905, 1298).

6-**Nitro**-2-**aminophenol** forms red needles, m.p. 110°–111° (Post and Stuckenberg, *l.c.*).

For a number of other mononitro-amino- and acetaminophenols, *see* Hahle, J. pr. Chem. 1891, [ii.] 43, 62; Kehrmann and Gauhe, Ber. 1898, 31, 2403; Meldola and Stephens, Chem. Soc. Trans. 1906, 923; *see* also J. Soc. Chem. Ind. 1905, 796).

When *p*-aminophenol is dissolved in a small quantity of glacial acetic acid, and acetic anhydride is added, the amino group is acetylated. To the solution at 0°, twice the calculated quantity of nitric acid (sp.gr. 1·5), diluted with twice the volume of acetic acid, is added in small portions at a time. The product is then poured into water and neutralised with ammonia, 2 : 6-*dinitro*-4-*acetaminophenol* is thus formed. It forms dense ochreous needles, m.p. 182° (Meldola and Hay, Chem. Soc. Trans. 1905, 1203).

When converted into its sodium derivative and reduced with aqueous sodium sulphide, it yields 2-*nitro*-6-*amino*-4-*acetaminophenol*

$$NHAc{\cdot}C_6H_2(NO_2)(NH_2)OH$$

brownish-red needles, m.p. 190°, which forms an orange-yellow diazo derivative when treated with nitrous acid (Cassella & Co. D. R. P. 172978, 1906).

4 : 6-**Dinitro**-2-**aminophenol** (*Picramic acid*) may be prepared by adding zinc-dust and

ammonia solution to a warm aqueous or methyl alcoholic solution of picric acid until the solution is distinctly alkaline. The mixture is boiled for an hour with occasional addition of ammonia, after which it is filtered, the excess of ammonia evaporated on the water-bath, and a slight excess of acetic acid is added. It is then evaporated to dryness, and the residue is recrystallised from boiling water. Or finely powdered picric acid (20 grams) is dissolved in 300 c.c. alcohol and 125 c.c. of ammonia (0·880) are added. After cooling to 30° hydrogen sulphide is passed in rapidly, so that the temperature rises to 50°–55° in 15 minutes. The solution is cooled and the stream of hydrogen sulphide continued for 45 minutes. Crystals of ammonium picramate are deposited; these are collected and decomposed by 60 c.c. acetic acid (1 part glacial acid to 4 parts water), and the picramic acid recrystallised from boiling water (Egerer, J. Biol. Chem. 1913, 35, 565). The acid forms fine red crystals, m.p. 165°, which burn, but do not detonate on sudden heating. It does not precipitate albumin, albumoses, peptone, or alkaloids. Its alkali salts yield deep red solutions, which are turned yellowish-green by acids, and may, therefore, be used as indicators in alkalimetry (Frébault and Aloy, J. Pharm. Chim. 1904, 20, 245; Bull. Soc. chim. 1905, [iii.] 33, 495; Borche and Heyde, Ber. 1905, 38, 3938).

Acetic anhydride reacts with sodium picramate at 60°, and the resulting product, when reduced at 80° by sodium sulphide, and then treated with acid, yields

4-Nitro-2-amino-6-acetaminophenol, which is hydrolysed by acids to 4-*nitro*-2 : 6-*diaminophenol*, the diazonium compound of the latter yielding azo dyes (Cassella, D. R. P. 161341; D. R. PP. 112819, 113241, 111327, 112280, 110711; Chem. Zentr. 1900, ii. 463, 509, 512, 547, 698).

2 : 6-**Dinitro-4-aminophenol** (iso*picramic acid*) forms thin yellow needles, m.p. 170° (decomp.). The corresponding acetamino derivative, treated with alkali sulphides, forms a compound which readily yields azo dyestuffs for wool, very fast to washing, milling, and light (Reverdin and Dresel, Ber. 1905, 38, 1593; Eng. Pat. 24409, 1903; J. Soc. Chem. Ind. 1904, 1025).

For other dinitroaminophenols, *see* Reverdin and Dresel, *l.c.*; Reverdin, Ber. 1907, 40, 2848; *ibid.* 1909, 42, 1523; Reverdin and Delétra, *ibid.* 1906, 39, 125; Meldola and Hay, Chem. Soc. Trans. 1907, 1481.

2 : 3 : 5-**Trinitro-4-acetaminophenol**

$$C_6H_2(OH)(NO_2)_3NH{\cdot}COCH_3$$

is obtained by nitrating diacetyl-*p*-aminophenol with cold fuming nitric acid, the mononitrodiacetyl derivative thus obtained is then further nitrated by dissolving it in a mixture of fuming nitric and strong sulphuric acid, when the above trinitro compound is formed. It crystallises in yellow needles, m.p. 178°–179° (decomp.), and owing to the great mobility of the meta- NO_2 group it forms a remarkably active synthetic agent (Meldola, Chem. Soc. Trans. 1906, 1935).

The acetyl group may be removed by dissolving it in concentrated sulphuric acid at the ordinary temperature, then placing the containing vessel in boiling water for a few minutes until a drop of the liquid, mixed with cold water, gives a red precipitate—if the latter is brown the reaction has gone too far and decomposition has set in. The liquid is cooled and poured on to ice. The *trinitroaminophenol* forms deep red needles decomposing at about 145°. It may be diazotised in the cold with sulphuric acid and sodium nitrite (Meldola and Hay, *ibid.* 1909, 1378; Meldola and Kuntzen, *ibid.* 1033; *ibid.* 1910, 444; *ibid.* Proc. 340).

2 : 4 : 6-**Trinitro-3-aminophenol**, m.p. 175°, may be obtained by the action of ammonia on 3-chloro-2 : 4 : 6-trinitrophenol (Blanksma, Ber. 1914, 47, 687).

NITROCRESOLS.

The cresols are directly nitrated with difficulty, a small yield of the mononitro products being obtained (Staedel, Annalen, 1883, 217, 49; Khotinsky and Jacopson-Jacopmann, Ber. 1909, 32, 3097; *cf.* Hollemann and Hoeflake, Rec. Trav. chim. 1917, 36, 271; Marqueyrol and Loriette, Bull. Soc. chim. 1919, [iv.] 25, 370). The alkali salts of their sulphonic acid derivatives may be converted into their mononitro derivatives much more readily; the HSO_3 group in the latter cannot, however, be eliminated, but by reduction they may be converted into the corresponding amino compounds which may be readily decomposed into aminocresols and sulphuric acid (Schultze, Ber. 1887, 20, 410).

3-**Nitro**-*o*-**cresol**

$$C_6H_3Me(OH)NO_2,(Me : OH : NO_2=1 : 2 : 3)$$

is obtained together with the 5-nitro derivative by dropping a glacial acetic acid solution of *o*-cresol into a cold mixture of 3 parts of nitric acid (sp.gr. 1·4) and 6 of acetic acid (Hirsch, *ibid.* 1885, 18, 1512; Noelting and Wild, *ibid.* 1339). It forms long yellow prisms, m.p. 69·5°, volatile in steam.

4-**Nitro**-*o*-**cresol** ($Me : OH : NO_2=1 : 2 : 4$) is best prepared by diazotising 4-nitro-2-toluidine in 10 p.c. sulphuric acid at 0°, and then dropping the product into boiling dilute sulphuric acid (Ullmann and Fitzenham, *ibid.* 1905, 38, 3799); it forms large yellow crystals, m.p. 118°.

5-**Nitro**-*o*-**cresol**, prepared by treating 5-nitro-2-toluidine with sodium nitrite and sulphuric acid, or with concentrated caustic soda, forms fine, white, silky needles which, when dried at 100°, have m.p. 94·6–95° (Neville and Winther, *ibid.* 1882, 15, 2978). It is also produced by the action of methyl ethyl ketone on nitromalonic aldehyde in alkaline solution (Hill, Amer. Chem. J., 1902, 24, 4).

6-**Nitro**-*o*-**cresol**, m.p. 142°–143°, having an intensely sweet smell, is formed from the corresponding nitrotoluidine by treating it with sodium nitrite and sulphuric acid (Ullmann, *ibid.* 1884, 17, 1961).

2-**Nitro**-*m*-**cresol** ($CH_3 : OH : NO_2=1 : 3 : 2$) is obtained, together with the 4- and 6-nitro derivatives, by nitrating *m*-cresol. It is volatile in steam and soluble in water, but has not been obtained pure. Its methyl ether forms colourless crystals, m.p. 88°–89° (Khotinsky and Jacopson-Jacopmann, *l.c.*).

4-**Nitro**-*m*-**cresol**, yellow crystals, m.p. 56°, is formed as above. The best yield of the 4-nitro derivative is obtained by nitrating at

$-8°$ to $-5°$ (*l.c.*). It is volatile in steam, but insoluble in water, and can thus be separated from the 2-nitro derivative.

5-Nitro-*m*-cresol, m.p. 60°–62°; 90°–91° when anhydrous, is obtained by treating 5-nitro-*m*-toluidine with nitric acid (Neville and Winther, *l.c.*).

6-Nitro-*m*-cresol, m.p. 129°, is obtained as above. It is volatile in steam, and can thus be separated from the 2- and 4-nitro derivatives.

2-Nitro-*p*-cresol ($CH_3 : OH : NO_2 = 1 : 4 : 2$) may be obtained by boiling diazotised 2-nitro-*p*-toluidine (Neville and Winther, *l.c.*), but it is best prepared by nitrating *p*-tolyl carbonate $CO(OC_7H_7)_2$ (m.p. 117°); the 2-nitro-*p*-tolyl carbonate $CO(OC_7H_6NO_2)_2$ thus obtained forms yellow needles, m.p. 143°–144°, which, when hydrolysed with boiling aqueous caustic soda, or sodium carbonate, yields the 2-nitro-*p*-cresol, yellow prisms, m.p. 77° (D. R. P. 206638; J. Soc. Chem. Ind. 1909, 328).

With fuming sulphuric acid 2-nitro-*p*-cresol yields acetyl acrylic acid (Schultz and Löw, Ber. 1909, 42, 577).

3-Nitro-*p*-cresol, formed by treating 3-nitro-*p*-toluidine with nitric acid or concentrated caustic soda, forms yellow needles, m.p. 33·5°, b.p. 125°/22 mm., 114·5°/7·5 mm., sp.gr. 1·2399 at 38·6°/4° (Noelting and Wild, *l.c.*; Brasch and Freyss, Ber. 1891, 24, 1960).

3 : 5-Dinitro-*o*-cresol

$$(CH_3 : OH : NO_2 : NO_2 = 1 : 2 : 3 : 5)$$

forms long yellow crystals, m.p. 86°–87° (Cazeneuve, Bull. Soc. chim. 1900, [iii.] 17, 201; Noelting and Salis, Ann. Chim. 1885, [vi.] 4, 105). Heated with ammonia at 180° it yields dinitrotoluidine (Barr. Ber. 1888, 21, 1543). It acts as a violent poison (Weyl, *ibid.* 1887, 20, 2835).

2 : 6-Dinitro-*p*-cresol, yellow needles, decomposes when heated, forming a violet sublimate (Knecht, Annalen, 1882, 215, 87).

3 : 5-Dinitro-*p*-cresol, m.p. 85°, is obtained by nitrating *p*-cresol in acetic acid solution with strong nitric acid (Frische, *ibid.* 1884, 224, 138; Staedl, *l.c.*; Chamberlain, Amer. Chem. J. 1897, 19, 533), and by a variety of other methods.

2[illegible] : 6-Trinitro-*m*-cresol, formed when *m*-cresol is nitrated, long, yellow needles, m.p. 109·5° (Murmann, Chem. Zentr. 1904, ii. 436; Noelting and Salis, Ber. 1881, 14, 987; and *l.c.*).

Tetranitro-*m*-cresol $CH_3{\cdot}C(OH)(NO_2)_4$, m.p. 175°, is converted into trinitroorcinol by boiling water (Blanksma, Proc. K. Akad. Wetensch, Amsterdam, 1906, 9, 278).

The relative sensitiveness to the shock of a falling weight of various metallic salts of trinitrophenol and cresol is discussed by Kast (Zeitsch. ges. chiess. and Sprengstoffw. 1911, 6, 7, 31, 67).

Dinitrocresol (Victoria yellow) is sometimes used for colouring food. It may be detected by digesting the finely-powdered sample of macaroni or other food with alcohol, filtering, evaporating to a small bulk and tasting—if it is bitter, picric acid is probably present. Then warm the solution for a few minutes with a little pure hydrochloric acid, cool and drop a fragment of zinc into the basin. After standing in the cold for ½–2 hours the solution will become bright blood-red if dinitrocresol is present, and a beautiful blue in the presence of picric acid (Fleck, J. Soc. Chem. Ind. 1887, 50).

Like the nitrophenols, the nitrocresols also form metallic, amino, and a variety of other derivatives.

2-Ethylphenol or **phlorol** forms one *mononitro*-derivative, a yellow oil, b.p. 212°–215°, and one *dinitro*- derivative (Behal and Choaz, Bull. Soc. chim. 1894, [iii.] 11, 309).

NITROXYLENOLS.

3 : 5-Dinitro-1 : 2 : 4-xylenol

$$C_6H(OH)(NO_2)_2(CH_3)_2(CH_3{:}CH_3{:}OH{:}NO_2{:}NO_2) = 1 : 2 : 4 : 3 : 5$$

forms yellow needles, m.p. 126°–127° (Noelting and Pick, Ber. 1888, 21, 3158).

5-Nitro-1 : 3 : 4-xylenol also forms yellow needles, m.p. 72° (Hodgkinson and Limpach, Chem. Soc. Trans. 1893, 105; Francke, Annalen, 1897, 296, 199).

Symmetrical xylenol has been nitrated by dissolving 5 grms. in 50 c.c. of equal parts of ordinary, and of 20 p.c. fuming, sulphuric acid, the solution is warmed for 15 minutes on the water-bath. After cooling 11·6 grms. of nitric acid of sp.gr. 1·415 are added, the whole, after standing, is warmed on the water-bath, and finally poured into 300 c.c. of water. The precipitate is filtered, washed, and dissolved in boiling water, and the potassium salt of the symmetrical trinitroxylenol is precipitated by adding potassium chloride in excess to the hot solution. It forms brown-yellow crystals, from which the free phenol may be liberated by boiling dilute hydrochloric acid. It forms colourless crystals, m.p. 104°, resembles picric acid in many respects, but is less soluble in water than picric acid and dyes wool in redder shades, whereas the corresponding trinitrocresol gives greenish-yellow colours. Unlike both these substances, it also gives no reaction with potassium cyanide (Knecht and Hibbert, Ber. 1904, 37, 3477; Blanksma, Rec. trav. chim. 20, 422).

Carvacrol forms a 5-*mononitro derivative*

$$CH_3(C_3H_7)C_6H_2{\cdot}NO_2(OH)(CH_3{:}C_3H_7{:}NO_2{:}OH = 1 : 4 : 5 : 2),$$

yellow crystals, m.p. 77°–78° (Mazara and Plancher, Gazz. chim. ital. 1891, 21, ii. 155), m.p. 87° (Kehrmann and Schön, Annalen, 1900, 310, 109); and a 3 : 5-*dinitrocarvacrol*, yellow needles, m.p. 117° (Dahmer, *ibid.* 1904, 333, 346).

Thymol yields an almost colourless 6-*nitrothymol*

$$CH_3(C_3H_7)C_6H_2(OH)NO_2(CH_3 : C_3H_7 : OH : NO_2 = 1 : 4 : 3 : 6)$$

m.p. 140° (Kehrmann and Schön, *l.c.* 107); a 2 : 6-*dinitrothymol*, m.p. 55° (Oliveri and Tortorici, Gazz. chim. ital. 1898, 28, i. 308).

2 : 5 : 6-*Trinitrothymol*, yellow needles, m.p. 110° (Maldotti, *ibid.* 1900, 30, ii. 365).

NITROCATECHOLS.

3-Nitrocatechol

$$C_6H_3(OH)_2NO_2(OH : OH : NO_2 = 1 : 2 : 3)$$

obtained by nitrating an ethereal solution of catechol with fuming nitric acid, forms long yellow needles, m.p. 86°, volatile in steam (Weselsky and Benedikt, Monatsh. 1882, 3, 386).

4-Nitrocatechol, yellow needles, m.p. 174°, may be prepared by treating catechol with potassium nitrite and dilute sulphuric acid (Benedikt, Ber. 1878, 11, 362), and by other methods (D. R. P. 81298; Frdl. iv. 121; Dakin, Amer. Chem. J. 1909, 42, 490). It is non-volatile in steam.

3 : 5-**Dinitrocatechol,** yellow needles, m.p. 164°, is formed by nitrating catechol diacetate with fuming nitric acid (Nietzki and Moll, Ber. 1893, 26, 2183).

NITRORESORCINOLS.

2-Nitroresorcinol

$C_6H_3(OH)_2NO_2(OH : OH : NO_2 = 1 : 3 : 2)$

may be prepared by adding 22 grms. of resorcinol to 150 c.c. of fuming sulphuric acid (sp.gr. 1·875), and warming on the water-bath; the 2 : 4-disulphonic acid thus formed is then nitrated with a mixture of 12·6 grms. nitric acid (sp.gr. 1·52), and 40 grms. of the fuming sulphuric acid. After 12 hours the mixture is poured into water and distilled with steam (D. R. P. 145190 of 1904). It forms crystals, m.p. 85°, and, when reduced with tin and hydrochloric acid, yields the corresponding amino derivative, whilst if reduced with iron and acetic acid, it forms chiefly benzoylaminoresorcinol

$C_6H_3(OH)_2NH(COC_6H_5)$

m.p. 187° (Kauffmann and Pay, Ber. 1906, 39, 323). It yields a nitroso, halogen, metallic, and other derivatives (Kauffmann and Franck, *ibid.* 2722; *ibid.* 1907, 40, 3999).

2-Nitroresorcinol may be coupled with diazonium chloride and azo dyes have been prepared from the resulting product (Kauffmann and Pay, *l.c.*).

4-Nitroresorcinol, m.p. 115°, is formed like the 2-nitro derivative (Ehrlich, Monatsh. 1887, 8, 426; Hemmelmayr, *ibid.* 1905, 26, 185).

5-Nitroresorcinol has m.p. 158° (Blanksma, Proc. K. Akad. Wetensch, Amsterdam, 1906, 9, 278).

2 : **4-Dinitroresorcinol** $C_6H_2(OH)_2(NO_2)_2$ may be obtained by treating the corresponding nitroso compound with cold nitric acid (sp.gr. 1·3) (Kostanecki and Feinstein, Ber. 1888, 21, 3122). It forms yellow needles, m.p. 147°–148° (Hemmelmayr, *l.c.*). For various derivatives and other methods of preparation, *see* Lippmann and Fleissner, Monatsh. 1887, 7, 98; Jackson and Koch, Amer. Chem. J. 1899, 21, 511; Jackson and Warren, *ibid.* 1891, 13, 179; *ibid.* 1904, 32, 297; Hemmelmayr, *l.c.*

4 : 6-**Dinitroresorcinol,** m.p. 214·5°, is formed by mixing resorcinol diacetate with 4–5 times its volume of well-cooled, fuming nitric acid (Schiaparelli and Abelli, Ber. 1883, 16, 872).

When 100 grms. of resorcinol is nitrated it yields a dinitro derivative, which, when stirred with 1000 grms. of 20 p.c. ammonia solution at ordinary temperature, yields a brown solution which soon deposits green crystals. The aqueous solution of the latter, when suitably thickened, printed on fabrics and steamed, gives brown shades very fast to soap and light. It can also be applied in conjunction with various acid and basic dyestuffs with or without mordants (D. R. P. 207465; J. Soc. Chem. Ind. 1909, 361).

Seven parts of mononitroresorcinol, heated with 10 parts of aniline, and 100 of hydrochloric acid for about an hour on the water-bath, yields a compound which dyes iron-mordanted tissues a greyish-blue and alumina mordanted tissues a blue shade.

Dinitroresorcinol (8 parts), similarly treated with 30 parts of resorcinol and 6 of hydrochloric acid, yields a dyestuff which dyes tissues mordanted with iron oxide, alumina or chromic oxide, yellowish-brown shades.

Mono- and dinitroresorcinol, heated alone with hydrochloric acid, also yield dyestuffs, which, however, are deficient in dyeing power (Poirrier and Ehrmann, Bull. Soc. Ind. Mulhouse, 1906, 76, 69).

2 : 4 : 6-**Trinitroresorcinol** (*Styphnic acid*) may be obtained by the prolonged action of nitric acid on various gums or resins; or on wood extracts (Bottger and Will, Annalen, 1846, 58, 269); by the action of fuming nitric acid on *m*-nitrophenol or on trinitrophenol (Bantlin, Ber. 1878, 11, 2101); by the action of a mixture of concentrated nitric and sulphuric acids on resorcinol (Merz and Zitter, Ber. 1879, 12, 681, 2037; *cf.* Guerewitsch, *ibid.* 1899, 32, 2425); by the oxidation of dinitroresorcinol (Fitz, *ibid.* 1875, 8, 631; Bendikt and Hübl, Monatsh. 1881, 2, 326) and by other methods.

Styphnic acid forms large yellow hexagonal crystals, m.p. 175·5°; is readily soluble in alcohol or in ether and in 88 parts of water at 62°. It gives a number of metallic salts, ethers, and molecular compounds with various organic compounds (Gibson, Chem. Soc. Trans. 1908, 2098; Ullmann and Bruck, Ber. 1908, 41, 3939). Alkylamine derivatives are described by Jerusalem (Chem. Soc. Trans. 1909, 1285).

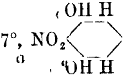
Tetranitroresorcinol has m.p. 152° (Blanksma, *l.c.*).

Hydroquinone or *quinol* (1 : 4-dihydroxybenzene) yields a *mononitro derivative*

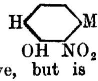
$C_6H_3(OH)_2NO_2$

m.p. 133°–134° (Elbs, J. pr. Chem. 1893, ii. 48, 179), and a 3 : 5-*dinitroquinol*, pale yellow leaflets, m.p. 135° (Shaw, Chem. Soc. Trans. 1911, 1609).

NITRO-ORCINOLS.

Mononitro-orcinol exists in two modifications: a- *derivative*, orange-coloured crystals, m.p. 127°, 

Me, is formed by the inter-action of an ethereal solution of orcinol and the molecular equivalent of fuming nitric acid (sp.gr. 1·515). Is volatile in steam.

β- Modification, m.p. 122°, 

Me, is formed like the a- derivative, but is non-volatile in steam. It forms brown crystals containing benzene of crystallisation, and yields green potassium and yellow silver salts (Henrich and Meyer, Ber. 1903, 36, 885).

2 : **4-Dinitro-orcinol** $C_6H(CH_3)(OH)_2(NO_2)_2$ forms deep yellow leaflets, m.p. 164·5° (Henrich, Monatsh. 1897, 18, 162); another dinitro-derivative known as **β-dinitro-orcinol,** m.p. 109°–110°, has also been described (Leeds, Ber. 1881, 14, 483).

Trinitro-orcinol $C_6CH_3(OH)_2(NO_2)_3$, formed by nitrating orcinol and also by other methods (Merz and Zeller, *ibid.* 1879, 12, 2038; Cazeneuve and Hugounenq, Bull. Soc. chim. 1888, 50, 643), long yellow needles, m.p. 162°–163·5° is feebly explosive above its melting-point.

NITROPYROGALLOLS.

5-Nitropyrogallol

$C_6H_2(OH)_3NO_2,H_2O(OH : OH : OH : NO_2 = 1 : 2 : 3 : 5)$

is obtained by the action of nitric acid on pyrogallol in ethereal solution at 0°. Forms brownish-yellow needles, or prisms which lose water of crystallisation at 100°, then melt at 205° (Barth, Monatsh. 1882, 1, 882).

4-Nitropyrogallol, m.p. 162°, is formed by boiling nitropyrogallol carbonate with water (Einhorn, Cobliner, and Pfeiffer, Ber. 1904, 37, 114).

4 : 6-Dinitropyrogallol, yellow needles, m.p. 208°, is formed by the action of a mixture of sulphuric and nitric acids on pyrogallol carbonate (Einhorn, Cobliner, and Pfeiffer, *l.c.*).

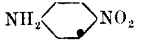
NITROPHLOROGLUCINOLS.

Phloroglucinol yields a **mononitro derivative** $C_6H_2(OH)_3(NO_2)(OH : OH : OH : NO_2 = 1 : 3 : 5 : 2)$ when nitrated with weak nitric acid. It forms reddish-yellow leaflets (Hlasiwetz, Annalen, 1861, 119, 200).

Trinitrophloroglucinol $C(OH)_3(NO_2)_3$ is formed by treating phloroglucinol triacetate or trimethyl phloroglucinol with fuming nitric acid (Nietzki and Mol, Ber. 1893, 26, 2185; Blanksma, *l.c.*). Yellow crystals; loses water of crystallisation at 100°, sublimes at 130°, m.p. 167° (anhydrous), explosive at higher temperatures.

A large number of halogen nitro derivatives of the nitrophenols and their homologues are known; for some recent literature, *see* Dahmer, *l.c.*; D. R. PP. 160304, 234742; J. Soc. Chem. Ind. 1905, 886; *ibid.* 1911, 884; Zincke and Klostermann, Ber. 1907, 40, 679; Heller, *ibid.* 1909, 41, 2191; and *l.c.*; Zincke and Breitweiser, *ibid.* 1911, 44, 176; Robertson, Chem. Soc. Trans. 1908, 788; Railford, Amer. Chem. J. 1910, 44, 209; *ibid.* 1911, 46, 417; Erp. Rec. trav. chim. 1910, ii. 14, 187; Zincke, Annalen, 1911, 381, 28.

NITRO-*m*-PHENYLENEDIAMINE.



Obtained by heating 4-nitroaniline-3-sulphonic acid with ammonia in an autoclave at 170°–180° (Aktienges. für Anilinfab. D. R. P. 130438). Also obtained by hydrolysing the nitrated diacetyl compound of *m*-phenylenediamine (Barbaglia, Ber. 1874, 7, 1257). M.p. 161°. Soluble in water, alcohol, or ether.

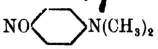
***p*-NITROPHENYLHYDRAZINE** *v.* HYDRAZINES.

NITROPHENYLHYDRAZONES *v.* HYDRAZONES.

***p*-NITROPHENYLNITROSAMINE** *v.* DIAZO-COMPOUNDS.

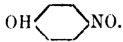
NITROSO COLOURING MATTERS *v.* QUINONEOXIME DYES.

***p*-NITROSODIMETHYLANILINE**



Prepared by adding an aqueous solution of sodium nitrite to a strongly cooled mixture of dimethylaniline and hydrochloric acid when the hydrochloride separates out as a yellow precipitate. M.p. 177°. Known commercially as Nitroso base *m*.

1-NITROSO-*β*-NAPHTHOL *v.* QUINONEOXIME DYES.

***p*-NITROSOPHENOL**  Obtained by adding dilute sulphuric acid to a phenol mixed with cold aqueous solutions of caustic soda and sodium nitrite. M.p. 126°.

NITROSOPHENOL and **NITROSOPHENOL COLOURING MATTERS** *v.* art. PHENOL AND ITS HOMOLOGUES.

NITROSTARCH *v.* EXPLOSIVES.

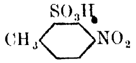
NITROSUGAR *v.* EXPLOSIVES.

'NITROSULPHATE' OF IRON *v.* arts. DYEING; IRON.

NITROSULPHURIC ACID *v.* SULPHUR.

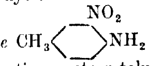
NITROTOLUENES *v.* BENZENE AND ITS HOMOLOGUES; TOLUENE.

***p*-NITROTOLUENESULPHONIC ACID**



Obtained by sulphonating *p*-nitrotoluene with fuming sulphuric acid on the water-bath and pouring the cooled mixture into water (Kastle, Amer. Chem. J. 1910, 44, 484; Dorssen, Rec. trav. chim. 1910, 29, 371). Pale yellow prisms from water, containing $2H_2O$. Used in the manufacture of Stilbene dyes.

NITROTOLUIDINES

m-*Nitro-p-toluidine* 

May be obtained by treating aceto-*p*-toluidide in sulphuric acid with a mixture of nitric and sulphuric acids and hydrolysing the product. M.p. 116°.

p-*Nitro-o-toluidine*.—Obtained by nitrating *o*-toluidine. For details of method employed on large scale, *see* Jansen, Zeitsch. Farb. Ind. 1913, 12, 181; quoted by Cain, Intermediate Products for Dyes, p. 96.

NITROXYLENES *v.* XYLENE.

NIZIN. Trade name for zinc sulphanilate.

NJAVE OIL *v.* OILS, FIXED, AND FATS.

NJIMO WOOD. This wood is obtained from the interior of the Cameroons, and contains a principle which is said to act like pepsin. The drug is found in commerce partly in billets with but little bark, partly as thick circular sections of the root uniformly covered with bark. The wood of both stem and root possesses a beautiful yellow colour, that of the former being dashed with red. It is easily reduced to powder with a rasp, and possesses an odour like musk. It contains numberless circular pores, which contain yellow resin. The alcoholic extract of the drug is yellow by transmitted light, but exhibits a green fluorescence resembling uranium glass. It appears to contain no alkaloid. The resin contains a bitter substance with a faint aromatic smell (Hugo Schulz, Pharm. Zeit. 31, 350; J. Soc. Chem. Ind. 5, 501).

NONANE C_9H_{20}. *n*-Nonane may be prepared from heptaldehyde, obtained by the distillation of castor oil, by acting on it with magnesium ethyl bromide whereby it is converted into ethyl-*n*-hexylcarbinol, from which γ-iodononane and *n*-Δ^{β}-*nonylene* may be obtained. *n*-Δ^{β}-*nonylene* is a colourless mobile liquid of pleasant, petroleum-like odour, b.p. 149·4°–149·9°, D^{15} 0·754. On passing its vapour mixed with hydrogen over freshly reduced nickel at 160°, *n*-nonane is formed. It is a mobile liquid of fragrant odour, b.p. 150·4°–150·6°/759 mm. D^{15}_{15} 0·7219, n^{25}_{D} 1·4025 (Clarke and Adams, J. Amer. Chem. Soc. 1915, 37, 2536).

Cyclo-**NONANONE** *v.* Azelaic acid.

NONDECATOIC ACID $CH_3[CH_2]_{17}COOH$ is obtained from octadecyl cyanide (Schweitzer, J. 1884, 1193); m.p. 66·5°, b.p. 297°–299° (100 mm.).

NONOIC ACIDS $C_9H_{18}O_2$.

1. *n-Nonoic acid* or *Pelargonic acid*

$$CH_3[CH_2]_7COOH$$

is contained as an ether in the oil from *Pelargonium roseum* (Pless, Annalen, 59, 54), and may be obtained by the oxidation of oil of rue (from *Ruta graveolens* [Linn.]) (Perrot, *ibid.* 105, 64), and of oleic acid (Redtenbacher, *ibid.* 59, 52) Also formed by the oxidation of stearolic acid ($C_{18}H_{32}O_2$) (Limpach, *ibid.* 190, 197); by boiling normal octyl cyanide with potash (Zincke and Franchimont, *ibid.* 164, 333); by melting undecylenic acid with potash (Krafft, Ber. 1882, 1691); and by heating the barium salt of sebacic acid with sodium methoxide (Mai, Ber. 1889, 2136); m.p. 12·5°, b.p. 253°–254°, sp.gr. 0·9068 at 170°/17°.

The characteristic odour of the quince is probably due to ethyl pelargonate. This ester (b.p. 227°–228°; sp. gr. 0·8655 17·5°/4°) is prepared commercially for flavouring common wines, brandy, &c., from the oxidised products of oil of rue.

2. iso*Nonoic acid, methylhexyl acetic acid*, or *a-methyloctoic acid* $CH_3[CH_2]_5CH(CH_3)COOH$ is formed by boiling methylhexyl carbinol cyanide with potash (Kullhem, Annalen, 173, 319); b.p. 244°–246° (corr.), sp.gr. 0·9032 at 18°/. Almost insoluble in water; readily soluble in alcohol and ether.

3. iso*Heptyl acetic acid* or *β-methyloctoic acid* $CH_3[CH_2]_5CH(CH_3)CH_2{\cdot}CO_2H$. Obtained by heating *iso*heptyl malonic acid; b.p. 232°. Insoluble in water; soluble in alcohol and ether (Venable, Ber. 13, 1652).

NONTRONITE. A hydrated ferric silicate of a light-green colour, which, on the expulsion of water, changes to a dark chestnut-brown; opaque, fracture uneven; lustre resinous; unctuous to the touch, and somewhat harder than talc. Specimens found at Heppenheim, in the Bergstrasse, and at Andreasberg gave numbers agreeing with the formula

$$Fe_2O_3{\cdot}3SiO_2,5H_2O$$

(Thorpe, Proc. Lit. and Phil. Soc. Manchester, 1869, 1).

NOPAL. The Mexican name of the cactaceous opuntia, upon which the cochineal insect (*Coccus cacti*) breeds.

NOR-ATROPINE, NOR-HYOSCYAMINE *v.* Tropeines.

NORDHAUSEN ACID. *Fuming oil of vitriol* or *pyrosulphuric acid v.* Sulphuric acid.

NORITE *v.* Gabbro.

NORMAL POWDER *v.* Explosives.

NORWAY SPRUCE RESIN *v.* Resins.

NOSEAN *v.* Lapis-lazuli.

NOSELITE *v.* Lapis-lazuli.

NOSOPHEN *v.* Synthetic drugs.

NOTTINGHAM WHITE. *Flake white v.* Pigments.

NOUMEITE *v.* Garnierite.

NOVACULITE *v.* Whetstone.

NOVAINE *v.* Carnitine.

NOVARGAN, NOVASPIRIN *v.* Synthetic drugs.

NOVATOPHAN. Trade name for ethyl 6-methyl-2-phenylquinoline-4-carboxylate.

NOVIFORM. Trade name for a bismuth compound of tetrabromopyrocatechol.

NOVOCAINE. Trade name for *p*-aminobenzoyldiethylaminoethanol hydrochloride, used as a substitute for cocaine. Fine white needles, m.p. 156°, very soluble in water (*v.* Synthetic drugs).

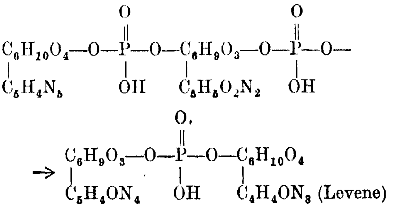
NOVOCOL. Trade name for sodium monoguaiacol phosphate.

NOVOJODIN *v.* Iodoform.

NOYAU *v.* Liqueurs and Cordials.

NUCIN or **JUGLONE.** This substance, obtained by Vogel and Reischauer from walnut husks, has been shown by Bernthsen to be an oxynaphthoquinone $C_{10}H_6O_3$ (Ber. 1884, 1945).

NUCLEIC ACID $C_{38}H_{50}O_{49}N_{15}P_4$, or



$$\begin{array}{cccccccc} & & O & & & & O & \\ & & \| & & & & \| & \\ C_6H_{10}O_4 & -O- & P & -O- & C_6H_9O_3 & -O- & P & -O- \\ | & & | & & | & & | & \\ C_5H_4N_5 & & OH & & C_5H_5O_2N_2 & & OH & \end{array}$$

$$\begin{array}{cccccc} & & & O & & \\ & & & \| & & \\ & C_6H_9O_3 & -O- & P & -O- & C_6H_{10}O_4 \\ \rightarrow & | & & | & & | \\ & C_5H_4ON_4 & & OH & & C_4H_4ON_3 \text{ (Levene)} \end{array}$$

A product of the degradation of the nucleoproteins of cell-nuclei; derived from yeast or from the thymus gland. That obtained from yeast is a white friable, tasteless odourless substance; practically insoluble in water but soluble in solutions of alkaline acetates; readily soluble in solutions of alkalis to form salts. From these solutions hydrochloric acid precipitates nucleic acid in dense curds, soluble in excess of the acid. In presence of a sufficient amount of alkaline acetate acids fail to precipitate nucleic acid. A solution of sodium nucleate gives with copper acetate solution acidified with acetic acid a greenish-blue precipitate; calcium chloride in excess in presence of acetic acid gives a white flocculent precipitate which quickly becomes granular. Silver nitrate in excess when added to a strong neutral solution of sodium nucleate gives a white gelatinous precipitate, soluble in sodium chloride forming an opaque colloidal solution. Aqueous solutions of sodium nucleate readily gelatinise, and, if concentrated, set to a jelly.

Nucleic acid of plant origin yields on hydrolysis guanine, adenine, cytosine, uracil, *d*-ribose (pentose), and phosphoric acid. That of animal origin forms guanine, adenine, cytosine, thymine, lævulinic acid (from a hexose), and phosphoric acid.

As used in medical practice it should be white, or at most, have a very faint buff colour. It should be completely soluble in an aqueous solution of sodium acetate or in dilute solutions of ammonia, or of sodium or potassium hydroxides. The precipitate, formed by the addition of hydrochloric acid to an aqueous solution of the sodium salt, should be completely soluble in an excess of the hydrochloric acid. At most, only traces of proteins should be present; a 5 p.c. solution in a small excess of ammonia when heated to 105° should give only a slight turbidity. It should contain not less than 15 p.c. of nitrogen (Kjeldahl process) and 9 p.c. of organic phosphorus, reckoned on the dry sample (Chapman, Analyst, 1918, 259). *See* PROTEINS.

NUN. This name is given to the fatty product of an insect found in Yucatan. It is a yellowish-brown fatty mass, which has a neutral reaction, absorbs oxygen from the air, melts at 48·9°, and resolidifies between 26·7° and 24·9°, dissolves easily in ether, benzene, chloroform, or oil of turpentine, but is insoluble in alcohol; saponifies with difficulty, yielding a pungent-smelling acid called *nŭc acid*, and a volatile oil, together with palmitic and stearic acid. Ammonia colours it red. Its solution in turpentine oil is converted, by exposure to the air, into a resinous syrup (A. Schott, Chem. News, 22, 110).

NUT-GALLS *v.* GALL-NUTS.

NUTMEG. The nutmeg is the kernel of the fruit of *Myristica fragrans* (Houtt) (*v.* Mace). When gathered the fruit is slowly dried, either in the sun or by artificial heat, the hard shell is removed and the nutmegs (except in the case of those from Penang) washed in milk of lime. The nuts are then sorted into grades according to their size, the larger and denser being the more valuable. Those which are shrivelled are reserved for the production of ground nutmeg, of which, however, little, if any, appears on the market.

The true nutmeg is oval or nearly spherical in shape, from 20 to 25 mm. long and from 15 to 18 mm. wide. It is wrinkled longitudinally with a groove marking the position of the raphe. In cross section it has a marbled appearance. It has a pleasant and characteristic odour and a hot aromatic taste.

Composition.—The preponderating constituents are a fixed oil, starch, albuminoids, and fibre; the flavour and therapeutic action are due to the volatile oil.

According to Winton, Ogden, and Mitchell (U.S. Dep. Agric. Bureau of Chemistry, Bulletin 66, 1902), nutmeg has the composition—

	Max.	Min.
Moisture	10·83	5·79
Ash, total	3·26	2·13
„ sol. in water	1·46	0·82
„ insol. in HCl	0·01	0·00
Ether extract, volatile	6·94	2·56
„ „ non-volatile	36·94	28·73
Alcohol extract	17·38	10·42
Reducing matter by acid conversion } calc. as starch	25·60	17·19
Starch by diastase method	24·20	14·62
Crude fibre	3·72	2·38
Nitrogen	1·12	1·05

(For earlier analyses by Richardson, *v.* U.S. Dept. of Agric. Div. of Chemistry, Bull. 13, pt. 2, 1887.)

The sole use of nutmeg is as a flavouring agent, but the volatile oil is employed in medicine as an aromatic and carminative. In large doses it produces epileptiform convulsions.

The expressed oil of nutmeg (*Adeps myristicae*) is used in plasters and hair lotions as a mild stimulant. It consists mainly of the fixed oil, but usually contains substantial proportions of the volatile oil also. When freed from this it has the following constants:—m.p. 29°–30°C.; saponification value, 184–186; iodine value, 56–59·5 (Parry, Food and Drugs, p. 235).

Adulteration.—As nutmegs are almost invariably sold whole, *i.e.* unground, adulteration is very rare in this country.

The substitution of the long nutmeg (*M. Argentea*) cannot be regarded as legitimate, being much inferior in flavour, still less that of wild nutmegs from *M. Malabarica* or other species of *Myristica*. Both would be detected at once by the complete absence of aroma, and also by their different shape and size. Worm-eaten nuts may be passed off as sound after stopping the holes and coating with lime. This will be revealed by careful inspection. More or less exhausted nuts may be detected by the reduced fat content.

Standards.—The United States standards for nutmeg are as follows: The fixed ether extract shall be not less than 25 p.c., the ash not greater than 5 p.c., the ash insoluble in hydrochloric acid not greater than 0·5 p.c., and the crude fibre not over 10 p.c. C. H. C.

NUTMEG BUTTER *v.* MYRISTICA FATS.

NUTMEG-OIL (sometimes called *Oil of Mace*) is obtained by subjecting crushed steamed nutmegs to a pressure of about 4000 lbs. per square inch at temperatures between 45° and 75° for about 20 hours. The amount of fat thus expressed varies with the origin and quality of the nutmegs, but in the case of Ceylon nutmegs it may amount to about 27 p.c. By extraction with ether the finely ground nutmegs afford nearly 43 p.c. of fat. The fat at ordinary temperatures is a soft brownish-yellow solid with the characteristic smell of nutmeg. It melts at 48°, and has a density of 0·9899 at 50°/50°, an acid value 11·2, a saponification value 174·6, and an iodine value 57·8. The fat extracted with ether melts at 50°; has a density of 0·9337 at 50°/50°, an acid value 12·9, saponification value 180·5, and iodine value 45·7 (Power and Salway, Chem. Soc. Trans. 1908, 93, 1654).

The expressed fat contains an *essential oil*, *trimyristin* $C_3H_5(C_{14}H_{27}O_2)_3$, a *phytosterol*, a substance of the formula $C_{18}H_{22}O_5$, *oleic* and *linolenic acids* as glycerides, small amounts of *formic*, *acetic*, and *cerotic acids*, together with unsaponifiable constituents and resinous material (*see* NUTMEG BUTTER, art. MYRISTICA FATS).

The *essential oil of nutmeg* has been examined by Power and Salway (Chem. Soc. Trans. 1907, 91, 2037—which also contains an account of the previous investigations of Gladstone, Wright, Brühl, Wallach, and Semmler on the subject, as well as references to its bibliography). It is a nearly colourless limpid liquid of sp.gr. 0·869 at 15°/15°, has an optical rotation of +38°·4 in a 1 dcm. tube, and is soluble in three times its volume of 90 p.c. alcohol. It consists of a mixture of *d-pinene* and *d-camphene*, together amounting to about 80 p.c.; *dipentene*, about 8 p.c.; *d-linalool*, *d-borneol*, *i-terpineol*, and *geraniol*, together about 6 p.c.; *myristicin* $C_{11}H_{12}O_3$ about 4 p.c.; together with small amounts of an *alcohol*, yielding on oxidation a *diketone* $C_8H_{14}O_2$; an *aldehyde* resembling citral, yielding a β-naphthacinchoninic acid derivative, m.p. 248°; *safrole*; *myristic*, *formic*, *acetic*, *butyric*, and *octoic acids*, and a *monocarboxylic acid* $C_{13}H_{18}O_3$ all as esters.

That portion of nutmeg oil which has been hitherto designated as 'myristicol' is a mixture of alcohols of which terpineol is the main constituent. As normal oil of nutmeg differs in its physical characters, particularly in optical rotatory power, its composition is evidently subject to considerable variation (Power and Salway). *See* OILS, ESSENTIAL.

NUTS. The name given to various seeds, some the produce of large trees, *e.g.* walnut, chestnut; others of shrubs, *e.g.* filbert; some even of small leguminous plants, *e.g.* pea nuts.

Nuts are, as a rule, rich in nitrogenous matter and in oil, and when palatable and digestible, afford a concentrated and nutritious food.

The following analyses, chiefly from American sources (Bull. 28, U.S. Dept. of Agric. 1899), will serve to show the average composition of the edible portions of many varieties of nuts:—

	Water	Protein	Fat	Carbo-hydrates	Ash
Almonds . .	4·8	21·0	54·9	17·3	2·0
Beechnuts .	4·0	21·9	57·4	13·2	3·5
Brazil nuts .	5·3	17·0	66·8	7·0	3·9
Chestnuts, fresh	45·0	6·2	5·4	42·1	1·3
Chestnuts, dried	5·9	10·7	7·0	74·2	2·2
Cocoanut . .	14·1	5·7	50·6	27·9	1·7
Filberts . .	3·7	15·6	65·3	13·0	2·4
Hickory nuts .	3·7	15·4	67·4	11·4	2·1
Pea nuts . .	9·2	25·4	38·6	24·4	2·0
Pecans . .	2·7	9·6	70·5	15·3	1·9
Pistachio nuts .	4·2	22·3	54·0	16·3	3·2
Walnuts . .	2·5	18·4	64·4	13·0	1·7

H. I.

NUX VOMICA, B. P.; U.S. P. (*Noix vomique*, Fr.; *Krahenaugen*, *Brechnuss*, Ger.). Among the numerous species of *Strychnos* distinguished for their toxic properties the best known is *S. Nux vomica* (Linn.), a medium-sized tree which is found throughout Southern and Eastern Asia and in the northern part of Australia. The seeds of the fruit of this tree constitute the nux vomica of commerce. They vary in size from 19 to 25 mm. diameter and 3 to 6 mm. thickness; are circular plano-convex or irregularly bent, greyish-green in colour with a satiny lustre. Internally they consist of a tough and horny albumen, in the centre of which is found a small embryo. They were introduced into Europe during the sixteenth and seventeenth centuries, and have gradually become an important article of *materia medica*. They are known in the market as 'Bombay,' 'Cochin,' and 'Madras' seeds. The finest specimens which have been examined are grown in Ceylon. In small doses nux vomica acts as a powerful nervous stimulant affecting certain nerve centres, particularly the medulla oblongata. Other parts of the tree possess similar physiological activity, notably the bark, which has attracted attention as an adulterant of cusparia or angustura and as such is called False Angustura Bark (*v.* CUSPARIA BARK). For further botanical and historical particulars, *v.* Flück. a. Hanb. 428; Bentl. a. Trim. 178; Oberlin and Schlagdenhauffen (J. Pharm. Chim. [iv.] 28, 225); Dunstan and Short (Pharm. J. [iii.] 13, 1053; 15, 1 and 156); Rosoll (Monatsh. 5, 94); Greenish (Pharm. J. [iii.] 15, 60); and Ford, Ho Kai and Crow (*ibid.* [iii.] 17, 927).

The poisonous action of nux vomica depends upon the presence of the two well-known bitter alkaloids, *strychnine* and *brucine*. The former was isolated from the seeds in 1818 by Pelletier and Caventou (Ann. Chim. [ii.] 10, 142; 26, 44), and the latter, a year later, from the bark and seeds, by the same chemists (*ibid.* [ii.] 12, 118; 26, 53). That strychnine is also present in the bark was shown by Shenstone in 1877 (Pharm. J. [iii.] 8, 445; 9, 154). These alkaloids are widely distributed among the species of the *Strychnos* genus. The *S. Ignatii* (Berg.), a climbing plant of the Philippine Islands, the seeds of which constitute the St. Ingatius' Beans, contains both alkaloids. Strychnine indeed was discovered by Pelletier and Caventou in the seeds of this plant (*cf.* Flückiger and Meyer, Pharm. J. [iii.] 12, 1; Flück. a. Hanb. 431; Bentl. a. Trim. 179; Crow, *ibid.* [iii.] 17, 970; and Ford, Ho Kai and Crow, *ibid.* [iii.] 18, 75). Strychnine and brucine are found also in *S. Tieuté* (Lesch.) of Java, the active ingredient in the Upas-Tieuté arrow poison (Pelletier and Caventou); in *Lignum colubrinum* or snakewood, from *S. colubrina* (Linn.), a Malabar tree (Berdenis, J. 1866, 710; H. G. Greenish, Pharm. J. [iii.] 9, 1014), and *S. Gauthieriana* (Piérre), the tree which yields the *hoang-nan* of China (*cf.* Planchon, J. Pharm. Chim. 1877, 384; Räber, Y.-Bk. Ph. 1881, 138). The Indian drug *bidara laut* derived from *S. ligustrina*, examined by H. G. Greenish, was found to contain brucine only (Pharm. J. [iii.] 9, 1013), while *S. blanda* from Burmah has been stated to contain neither strychnine nor brucine (Small, Pharm. J. [iv.] 36, 510, 522; Kew Bull. 4 and 5, 1917, 121). Other poisonous species of *Strychnos* depend upon the alkaloid curarine for their activity (*v.* CURARA); and the African shrub *akazga*, apparently belonging to the same genus, contains a nearly related base *akazgine* (Frazer, J. pr. Chem. 104, [i.] 51).

Strychnine $C_{21}H_{22}O_2N_2$, the principal alkaloid of *Strychnos Nux-vomica* (Linn.), *S. Ignatii* (Berg.), *S. colubrina* (Linn.), *S. Tieuté* (Lesch.), and other *Strychnos* spp. The nearly allied alkaloid brucine usually occurs with strychnine in these plants, but *S. Rheedei* contains brucine only. The seeds of the first two alone are used as sources of strychnine. The seeds of *S. Nux-vomica* vary in the amount of total alkaloid (strychnine and brucine) they contain. As little as 1 p.c. has been found, and as much as 5 p.c. in the seeds of the Ceylon nux vomica, but probably 2·5 p.c. may be regarded as a reasonable commercial average. The official requirement in regard to alkaloidal content in the British and United States Pharmacopœias is 1·25 p.c. of strychnine determined in a specific manner, which in the case of the former is as follows:—7·5 grms. of the seeds in No. 60 powder are shaken well and frequently during thirty minutes with a mixture of 25 c.c. chloroform, 50 c.c. ether, and 5 c.c. ammonia solution. 50 c.c. (=5 grms. of seeds) of the clear ethereal extract is transferred to a separator and agitated with three successive portions, each of 10 c.c., of N-sulphuric acid. The united acid washings are made alkaline with ammonia and extracted with 10, 5 and 5 c.c. of chloroform. The chloroform is then removed by distillation and the alkaloidal residue dissolved in 15 c.c. of sulphuric acid 3½ p.c., this solution is heated to 50°C. and 3 c.c. of a mixture of equal volumes of nitric acid and water added, and set aside for ten minutes This acid liquid is then made alkaline with excess of sodium hydroxide and successively shaken with 10, 5 and 5 c.c. of chloroform, the chloroform extract being 'scrubbed' through 5 c.c. of water, and distilled, adding towards the end 5 c.c. of alcohol. After complete distillation, the residue is dried at 100° and weighed; this should be 0·06 to 0·065 grm =1·2 to 1·3 p.c. Tincture of Nux Vomica is standardised in the British and United States Pharmacopœias respectively to contain 0·125 and 0·1 grm. of strychnine in 100 c c., and may be assayed as follows:—100 c.c. are evaporated on the water-bath to a syrupy extract, washed with 20 c.c water into a separator, 5 grms. of sodium carbonate in 25 c.c. water added and the mixture agitated successively with 10, 10 and 10 c c. of chloroform. Proceed then as in the case of the 50 c.c of ethereal extract in the assay of the powdered seeds. Extract of Nux Vomica is standardised to contain 5 p.c. of strychnine in both the British and United States Pharmacopœias; whereas the Fluid Extract should contain 1·5 grms. of strychnine per 100 c.c. in the British, but only 1 grm. per 100 cc. in the United States Pharmacopœia. For the assay of the extract 3 grms.—or of the fluid extract 10 c.c.—may be taken, the process being substantially that followed in the case of the tincture. About one-third of the total alkaloid is strychnine and two-thirds brucine (Dunstan and Short, *ibid.* 1882–1883, [iii.] 13, 1053; 1884–1885, 15, 1). The total alkaloids from the seeds of *S. Ignatii* are richer in strychnine than those of *S. Nux-vomica.* The leaves of *S. Nux-vomica* contain *strychnicine*, needles, m.p. 240° (van Boorsma, Bull. Inst. bot. Buit. 1902, 14, 3).

Preparation.—The following process may be used for the extraction of strychnine and brucine from the seeds of *S. Nux-vomica* or *S. Ignatii.* The finely-powdered seeds are made into a paste with water and one-fourth of their weight of slaked lime. The mixture is thoroughly dried on the water-bath, and the dry mass finely powdered. The alkaloids are now dissolved from it by hot percolation with a suitable solvent (amyl alcohol, benzene, or chloroform) in an extraction apparatus. The solvent is shaken with dilute sulphuric acid, which removes the alkaloids as sulphates. These salts may be crystallised from the neutral solution, or the alkaloids may be regenerated, and the mixture (strychnine and brucine) extracted with dilute (25 p.c.) alcohol, which dissolves the brucine, and leaves nearly the whole of the strychnine undissolved. It is purified by recrystallisation from alcohol.

Properties.—Rhombic prisms, m.p. 268° (Loebisch and Schoop, Monatsh. 1885, 6, 858). At higher temperatures some of the alkaloid sublimes unchanged. According to Loebisch (*l.c.*), the alkaloid distils without decomposition at 270° under 5 mm. pressure. Lævorotatory, $[\alpha]_D - 36°$ in neutral salts (Tykociner, Rec. trav. chim. 1882, 1, 46). Very slightly soluble in water (1 in 6667, at 15°; 1 in 2500 at 100°). The aqueous solution is alkaline, and even when largely diluted, has a persistent bitter taste; the bitterness is perceptible in a solution containing 1 part of strychnine in 700,000 parts of water. The alkaloid is sparingly soluble in absolute alcohol (0·302 in 100 at 8·25°), ether (1 in 5500 at 25°), but is dissolved by chloroform (1 in 6), benzene (1 in 150 at 25°), amyl alcohol (1 in 180 at 25°), or 90 p.c. alcohol (1 in 170).

Strychnine is a violent poison, giving rise to tetanic spasms, owing to the greatly increased excitability of the spinal cord. Half a grain of the alkaloid has proved fatal to man.

Strychnine is a monacidic base: its salts are, as a rule, crystalline and soluble in water. The hydrochloride $B \cdot HCl, 2H_2O$ forms small colourless prisms, and is soluble in 35 parts of cold water; the nitrate $B \cdot HNO_3$ forms colourless, glancing prisms, and is soluble in 80 parts of water at 18°–19°; the sulphate $B_2 \cdot H_2SO_4, 5H_2O$ forms colourless prisms, soluble in 31 parts of water at 25°. All these salts are neutral in aqueous solution.

Reactions and Detection.—Strychnine, which is one of the most stable of alkaloids, is not coloured by sulphuric acid, and gives at most only a yellow coloration with nitric acid. It may be heated to 100° with sulphuric acid without being appreciably affected. When brought into contact with certain oxidising agents it exhibits a striking colour reaction, which is generally relied on for its detection. If the alkaloid is dissolved in a drop of strong sulphuric acid, and a small piece of potassium dichromate, manganese dioxide, ceric oxide, or potassium permanganate is stirred into the mixture, a play of colours is observed, beginning with blue, which gradually passes through violet and red to yellow (Marchand, J. Pharm. Chim. [iii.] 4, 200). The only other alkaloids which behave exactly like strychnine in this respect are curarine and gelsemine. Several alkaloids, however, give a somewhat similar colour reaction, but most of these are coloured by sulphuric acid alone, and may thus be readily distinguished from strychnine. The presence of foreign organic compounds frequently obscures the colour, and the alkaloid to be tested must, therefore, first be isolated in a nearly pure state, and separated, as far as possible, from any other alkaloid that may be present. This colour reaction cannot be obtained in the presence of much brucine, the alkaloid which accompanies strychnine in the plant, since it gives a deep-red coloration when oxidised which obscures the play of colours produced by the strychnine. This alkaloid may, however, be removed by oxidation with dilute nitric acid, the strychnine being recovered from the acid liquid by adding ammonia and extracting with chloroform (Shenstone, Pharm. J. 1877-1878, [iii.] 8, 445; Hanriot, Compt. rend.

1883, 97, 267), or the mixed alkaloids may be washed with chlorine water, when the brucine is converted into the soluble dichlorobrucine, which dissolves, leaving a residue of strychnine (Beckurts, Arch. Pharm. 1890, 228, 326). In toxicology, where traces of impurity in the alkaloidal residue would give rise to darkening when the sulphuric acid is added, the residue may be moistened with the strong acid and heated on the water-bath until the impurity is completely decomposed; water is then added, and the strychnine recovered by adding ammonia and extracting with chloroform.

Brucine $C_{23}H_{26}O_4N_2$. This alkaloid occurs with strychnine in *S. Nux-vomica* (Linn.) and in other species of *Strychnos*. In the seeds of *S. Nux vomica* about two-thirds of the total alkaloid is brucine (Dunstan and Short, Pharm. J. 1884–1885, [iii.] 15, 1). In the seeds of *S. Ignatii* the proportion of brucine appears to be smaller.

Preparation.—The total alkaloid having been extracted from the plant by the method described for strychnine, the mixture is repeatedly washed with dilute alcohol (25 p.c. by volume) and the brucine crystallised from the solution, and recrystallised several times from the same solvent or from water, the fractions which crystallise latest being almost, if not quite, pure brucine.

According to Flückiger (Pharm. Chem.), if the mixture of the two alkaloids is converted into the acetates and the solution is evaporated to dryness on the water-bath the strychnine acetate undergoes dissociation into the alkaloid and acetic acid, which volatilises. The brucine acetate remains unchanged, and may be dissolved from the residue by cold water and crystallised. For another method which is said to furnish quite pure brucine, *see* Shenstone, Chem. Soc. Trans. 1881, 39, 453.

Properties.—Brucine separates from its solutions in water or aqueous alcohol in monoclinic prisms containing $4H_2O$, m.p. 105°, or with $2H_2O$ from alcohol (Moufang and Tafel, Annalen, 1899, 304, 24). The crystals lose their water at 100°, or on standing over sulphuric acid. The anhydrous substance melts at 178° (Claus, Ber. 1881, 14, 773); lævorotatory, $[\alpha]_D$=in alcohol −85°, in chloroform −119° to 127° (Oudemans, Annalen, 1873, 166, 69). Slightly soluble in cold water (1 in 320), twice as soluble in boiling water, very soluble in alcohol, chloroform, or amyl alcohol; insoluble in ether. Brucine and its salts are bitter, and when subcutaneously injected in animals produce a physiological action resembling in kind that of strychnine, but much feebler. When administered internally to animals it produces little or no effect, owing chiefly to the rapidity with which it is eliminated (Brunton, Chem. Soc. Trans. 1885, 47, 143).

Brucine is a monacidic tertiary base; the ordinary salts are crystalline, and readily dissolve in water.

Reactions.—Brucine is readily distinguished from strychnine, since it does not give rise to the characteristic play of colours when oxidised with chromic acid, &c., only an intense red coloration being produced, whilst brucine is further differentiated from strychnine by giving a deep-red coloration when mixed with nitric acid; this is a very delicate test for brucine, and conversely for nitric acid. This red coloration of brucine is distinguished from that produced when some other alkaloids (*e.g.* morphine) are mixed with nitric acid, by the action of stannous chloride or certain other reducing agents, which when cautiously added change the red coloration to violet. (*Cf.* Wöber, Zeitsch. angew. Chem. 1918, 31, 124; Analyst, 1918, 350.)

When heated with strong hydrochloric acid brucine evolves two molecular proportions of methyl chloride (Shenstone, Chem. Soc. Trans. 1883, 43, 101; Hanssen, Ber. 1884, 17, 226).

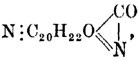
Detection and estimation.—Brucine may be detected by means of the properties and reactions described above. It may be estimated in plants and in medicinal preparations by the methods described in connection with strychnine (p. 617).

Constitution of strychnine and brucine. In spite of the fact that these two alkaloids were isolated more than a century ago it is only quite recently that it has been possible to put forward constitutional formulæ for them. The principal facts so far ascertained in the chemistry of these alkaloids, and which bear directly on the problem of their constitution, are as follows:—

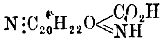
Both alkaloids contain two atoms of nitrogen, but behave as tertiary monacidic bases and contain no methyl linked to nitrogen. On treatment with alkalis they each take up 1 mol. of water and form *strychninic* and *brucinic acids* respectively.

Brucine differs from strychnine by $(\cdot OCH_2)_2$, and in yielding 2 mols. of methyl iodide or methyl chloride when heated with concentrated hydriodic or hydrochloric acid. Apart from this the reactions of brucine are exactly parallel with those of strychnine, and the whole series of brucine derivatives correspond with those of strychnine and show a constant difference $(\cdot OCH_2)_2$.

These facts warrant the following assumptions: (1) Of the two nitrogen atoms one is present as an imino group: N·CO, and this is converted into: NH·COOH in the transformation of strychnine

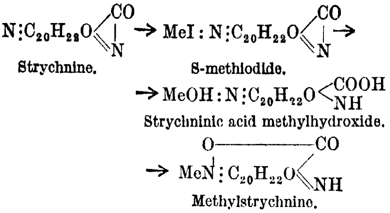


$N\vdots C_{20}H_{22}O\left\langle\begin{matrix}CO\\ |\\ N\end{matrix}\right.$, into strychninic acid



$N\vdots C_{20}H_{22}O\left\langle\begin{matrix}CO_2H\\ NH\end{matrix}\right.$ and of brucine into brucinic acid. The N- atom concerned in the change is devoid of basic properties, and consequently the alkaloids are monacidic, this property depending on the second nitrogen atom. (2) Since the second nitrogen atom is tertiary, and yet has no methyl group attached, it must be linked up with a third carbon atom in a ring. (3) Brucine is probably a dimethoxy-derivative of strychnine.

On treatment with methyl iodide strychnine forms a methiodide, which, when warmed with barium hydroxide, forms methylstrychnine, which behaves as a betaïne and is a secondary base; thus it furnishes a nitrosoamine and reacts with methyl iodide to form dimethylstrychnine, a substance which closely resembles N-methyltetrahydroquinoline in its properties, whence it may be concluded that strychnine contains a reduced quinoline nucleus. These changes may be represented thus—



Strychnine. S-methiodide. Strychninic acid methylhydroxide. Methylstrychnine.

The conclusion that strychnine contains a quinoline nucleus receives confirmation from the fact that the alkaloid is readily nitrated and sulphonated, and that on treatment with nitric acid it yields dinitrostrycholcarboxylic acid, which by loss of CO_2 passes into dinitrostrychol, which appears to be a dinitrodihydroxyquinoline $(NO_2)_2C_9H_3N(OH)_2$.

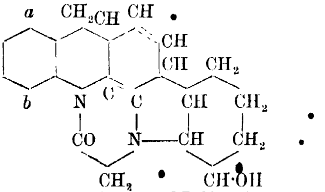
The study of the oxidation products of strychnine and brucine has also afforded useful data. When either alkaloid is oxidised with chromic acid it furnishes an acid

$$C_{15}H_{17}O_2N_2(COOH)$$

which contains no methoxyl, so that in the formation of this acid it must be the portion of the molecule containing the two $\cdot OCH_3$ groups of brucine that has been destroyed thus—

$C_{15}H_{17}O_2N_2\cdot C_6H_5$ Strychnine $C_{15}H_{17}O_2N_2\cdot C_6H_3(OMe)_2$ Brucine.

The yield of this acid is unfortunately small, but on distillation with zinc-dust it yields diphenylimide (carbazole), a substance which also occurs among the products of the destructive distillation of strychnine. On the basis of these results Perkin and Robinson have suggested that strychnine and brucine must contain both a quinoline and a carbazole nucleus (Chem. Soc. Trans. 1910, 97, 305) and have suggested the following formula for strychnine—



Strychnine (Perkin and Robinson).

The formula for brucine differs from this only in having methoxyl groups substituted at positions *a* and *b*.

The principal papers relating to the chemistry of strychnine and brucine are as follows: Gerhardt, Annalen, 1842, 44, 270; Compt. rend. 1844, 19, 1105; Nicholson and Abel, Chem. Soc. Trans. 1850, 2, 241; Schützenberger, J. 1858, 373; Stahlschmidt, *ibid.* 1859, 395; Gal and Etard, *ibid.* 1878, 910; 1879, 820; Bull. Soc. chim. 1879, [ii] 31, 98; Schiff, J. 1878, 910; Claus and collaborators, Ber. 1881, 14, 766, 774; Shenstone, Chem. Soc. Trans. 1881, 39, 456; 1883, 43, 101; 1885, 47, 139; Oechsner de Coninck, Compt. rend. 1882, 95, 298; 1884, 99, 1077; Hanriot, *ibid.* 1883, 96, 1671; Bull. Soc. chim. 1884, [ii.] 41, 235; Plugge, Ber. 1883, 16, 2683; Hanssen, *ibid.* 1884, 17, 2266, 2849; 1885, 18, 293, 777, 1917; 1886, 19, 521; 1887, 20, 451; Loebisch and Schoop, Monatsh. 1885, 6, 855; 1886, 7, 76, 709; 1888, 9, 629; Stoehr, Ber. 1885, 18, 3429; 1887, 20, 810, 1108, 2727; J. pr. Chem. 1890, [ii] 42, 405; Tafel, Ber. 1890, 23, 2734; 1892, 25, 412; 1893, 26, 333; 1900, 33, 2216; Annalen, 1891, 264, 33; 1892, 268, 229; 1898, 301, 285; with Moufang, 1899, 304, 26; with Naumann, Ber. 1901, 34, 3291; Leuchs and collaborators, *ibid.* 1908, 41, 1711, 4393; 1909, 42, 770, 2494, 2681, 3067, 3703; 1910, 43, 1042, 2362, 2417; 1911, 44, 2136, 3040; 1912, 45, 201; 1913, 46, 3693, 3917; 1914, 47, 370, 536; 1915, 48, 1009; 1918, 51, 1375; 1919, 52, 1443 and 2195; 1921, 54, 2177; 1922, 55, 564 and 724; Perkin and Robinson, Chem. Soc. Trans. 1910, 97, 305 (this paper gives a résumé of the principal facts bearing on the constitution of strychnine and brucine); Pictet and collaborators, Ber. 1905, 38, 2782, 2787; 1907, 40, 1172.

'Igasurine,' a supposed third alkaloid in nux vomica, was reported by Desnoix (J. Pharm. Chim. [iii.] 25, 202) and Schützenberger (Compt. rend. 46, 1234), but this was subsequently shown by Jorgensen (J. pr. Chem. [ii.] 3, 175) and Shenstone (Chem. Soc. Trans. 37, 235; 39, 453) to be impure brucine. Other constituents are *igasuric acid* (Pelletier and Caventon, Ann. Chim. [ii.] 10, 167; 26, 54), probably a variety of tannic acid (Ludwig, Arch. Pharm. [iii.] 2, 137; Carriol, J. Pharm. Chim. 19, 155; Marsson, Annalen, 72, 296; Sander, Arch. Pharm. 235, 133), but according to Gorter (*ibid.* 247, 197) identical with *chlorogenic* acid $C_{32}H_{28}O_{19}$ from coffee berries. Loganin, colourless prisms, m.p. 215°, occurs in the pulp of the fruit of Ceylon nux vomica to the extent of 5 p.c., and on acid hydrolysis yields glucose and *loganetin*, Dunstan and Short (Pharm. J. 1884, 1025); 11 p.c. of proteids (Fluck. a. Hanb. Pharmacographia); mucilage; sugar; and about 4 p.c. of a fatty oil (*ibid.*). Meyer (J. 1875, 856); Greenish (Pharm. J. [iii.] 12, 581); Dunstan and Short, Harvey and Wilkes (J. Soc. Chem. Ind. 24, 718), Watt and Angus (*ibid.* 35, 1916, 201).

H. E. W.

NYCANTHES ARBOR-TRISTIS (Linn.). This is a large shrub with rough leaves and sweet scented flowers occurring in the sub-Himalayan and Tarai tracts; also in Central India, Burmah, and Ceylon. The flowers open towards evening and fall to the ground on the following morning. The corolla tubes are orange coloured and give a beautiful but fleeting dye, which is mostly used for silk, sometimes in conjunction with 'kusum' or turmeric, occasionally with indigo and kath (Watts, Dict. Econ. Prod. of India, 1891, 5, 434).

According to Hill and Sirkar (Chem. Soc. Trans. 1907, 91, 1501) these flowers yield a red crystalline colouring matter *nycanthin*. An aqueous decoction treated with 1 p.c. of hydrochloric acid, is warmed gently for several hours, the precipitate collected and extracted with boiling alcohol. The extract heated with 1 p.c. hydrochloric acid deposits the colouring matter in red flakes which are washed with alcohol, and crystallised from pyridine or phenylhydrazine.

Nycanthin separates from pyridine in minute regular hexagons, and from phenylhydrazine in rhombic crystals; these are yellow, while wet, but brick red when dry, and melt at

285°–287° (Perkin, Chem. Soc. Trans. 1912, 101, 1539). It dissolves in alkalis to form a yellow solution from which it appears to be reprecipitated unchanged by acids, and contains no methoxyl group. With sulphuric acid it gives a most intense blue colour, which, however, rapidly turns yellow, and in this respect resembles bixin, the colouring matter of annatto (*Bixa Orellana* [Linn.]).

The analyses of Hill and Sirkar (*l.c.*) agree closely with $C_{20}H_{27}O_4$ or $C_{15}H_{20}O_3$, but of these formulæ the former appears to be preferable. *Acetylnycanthin* $C_{20}H_{26}O_4 \cdot C_2H_3O$, and the bromine compound $C_{20}H_{15}O_{18}Br_5$, amorphous powders, have been prepared by these authors. Mannitol was also isolated from the flowers.

For dyeing purposes the material (silk or cotton) is simply steeped in a hot or cold decoction of the flowers. The addition of alum and lime juice to the dye-bath is said to render the colour more permanent.

According to Perkin (private communication) the flowers of the *Cedrela Toona* (Roxb.), also employed as a dyestuff in India, yield a small quantity of crystalline red colouring matter, which closely resembles and is probably identical with nycanthin.

A. G. P.

O.

OAK-BARK. The oak tree is generally barked from the beginning of May till the middle of July. The barkers make a longitudinal incision with a mallet furnished with a sharp edge, and a peculiar incision by means of a barking-bill. The bark is then removed by peeling-irons, the separation being promoted, when necessary, by beating the bark. It is stacked in pieces about 2 feet long (*v.* LEATHER). Oak-bark tannin contains no methoxyl group and the methoxy- compounds associated with it have no tanning properties. No compound is to be found in the bark from which tannin might be produced.

OAK-GALLS *v.* GALL NUTS.

OAK-LEAVES. The leaves of *Quercus sessiliflora* contain minute quantities of methyl alcohol, hexenol, and lower homologues and higher unsaturated alcohols, formic, acetic, and higher unsaturated acids and a variety of aldehydes (Franzen, Zeitsch. physiol. Chem. 1921, 112, 301).

OAK-VARNISH *v.* VARNISH.

OATS *v.* CEREALS.

OBLITINE *v.* CARNITINE.

OBREGUIN. A substance intermediate in character between the fats and resins, occurring in Mexico on the twigs of *Althaea rosea* (Cav.). Nearly insoluble in water; easily soluble in ether, chloroform, or turpentine oil. On evaporation its solutions form a colourless, odourless mass, of the consistency of turpentine. Saponifiable by alkalis.

OBSIDIAN (Fr. *Obsidienne*). A glassy volcanic rock, generally jet-black or of dark bottle-green tint, and nearly opaque, except on the thin edges, which are translucent. Obsidian results from the rapid cooling of lavas of the acid type; the corresponding glass in the basic series being termed *tachylyte*. Microscopic examination of obsidian usually reveals the presence of numerous enclosures, known as crystallites and microlites, which are arranged in bands, indicating a flow structure. An analysis of obsidian from Obsidian Cliff, Yellowstone National Park, Wyoming, gave: SiO_2 74·70, Al_2O_3 13·72, Fe_2O_3 1·01, FeO 0·62, MnO trace, CaO 0·78, MgO 0·14, K_2O 4·02, Na_2O 3·90, H_2O 0·62, FeS_2 0·40 =99·91; sp.gr. 2·34. This composition is also that of a granite and a rhyolite. Other well-known localities are Iceland and the Lipari Islands. Obsidian being a homogeneous glass breaks with a typically conchoidal fracture. It can be chipped and flaked with sharp-cutting edges, and hence in parts of Mexico where the material is abundant, as at the Cerro de las Navajas ('Hill of Knives'), it was used by the Aztecs for knives, razors, and arrow-heads. It has also been employed by savages in other volcanic countries. Obsidian has occasionally been cut and polished as a gem-stone, but displays too little colour, even when thin, and is, moreover, too soft for general use. The hardness is somewhat higher than that of window-glass. A variety with a rich silvery sheen is, however, used for ornamental purposes in the Caucasus, while a brownish-red streaked variety, known as 'mahogany-obsidian,' has been employed to a limited extent as a decorative material in the United States. On Obsidian Cliff, Yellowstone National Park, *v.* J. P. Iddings, Seventh Ann. Rep. U.S. Geol. Survey, 1888.

L. J. S.

OCCLUSION (*occludo*, to enclose). Graham's term for the process of absorption or condensation of gases within the pores of a substance, *e.g.* the absorption of hydrogen by platinum and palladium, or the condensation of marsh-gas or fire-damp in coal.

OCHRE. A name applied to various native pigments, distinguished according to colour as yellow, brown, and red ochres, and consisting essentially of ferric hydroxides (represented by the mineral species limonite and turite), usually more or less earthy by admixture with clay, or sand. When containing much manganese they pass into umber (*q.v.*). Deposits of fine yellow ochre occur in the Lower Greensand of Shotover Hill, near Oxford. Red and brown ochres are commonly associated with iron-ores, especially with the hæmatite occurring in pockets in the Carboniferous Limestone, and have been worked in South Wales, the Forest of Dean, near Bristol, at Brixham in Devonshire, Ulverston in Lancashire, and near Workington in Cumberland. Some of the finest ochres of commerce are obtained from France, and are known as Auxerre and Rochelle ochres. In the United States, ochres are worked in connection with many deposits of iron-ore, especially in Virginia and Pennsylvania. Ochre is deposited by the water of chalybeate springs and by the waters

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OBLITINE *v.* CARNITINE.

OBREGUIN. A substance intermediate in character between the fats and resins, occurring in Mexico on the twigs of *Althaea rosea* (Cav.). Nearly insoluble in water; easily soluble in ether, chloroform, or turpentine oil. On evaporation its solutions form a colourless, odourless mass, of the consistency of turpentine. Saponifiable by alkalis.

OBSIDIAN (Fr. *Obsidienne*). A glassy volcanic rock, generally jet-black or of dark bottle-green tint, and nearly opaque, except on the thin edges, which are translucent. Obsidian results from the rapid cooling of lavas of the acid type; the corresponding glass in the basic series being termed *tachylyte*. Microscopic examination of obsidian usually reveals the presence of numerous enclosures, known as crystallites and microlites, which are arranged in bands, indicating a flow structure. An analysis of obsidian from Obsidian Cliff, Yellowstone National Park, Wyoming, gave: SiO_2 74·70, Al_2O_3 13·72, Fe_2O_3 1·01, FeO 0·62, MnO trace, CaO 0·78, MgO 0·14, K_2O 4·02, Na_2O 3·90, H_2O 0·62, FeS_2 0·40 = 99·91; sp.gr. 2·34. This composition is also that of a granite and a rhyolite. Other well-known localities are Iceland and the Lipari Islands. Obsidian being a homogeneous glass breaks with a typically conchoidal fracture. It can be chipped and flaked with sharp-cutting edges, and hence in parts of Mexico where the material is abundant, as at the Cerro de las Navajas ('Hill of Knives'), it was used by the Aztecs for knives, razors, and arrow-heads. It has also been employed by savages in other volcanic countries. Obsidian has occasionally been cut and polished as a gem-stone, but displays too little colour, even when thin, and is, moreover, too soft for general use. The hardness is somewhat higher than that of window-glass. A variety with a rich silvery sheen is, however, used for ornamental purposes in the Caucasus, while a brownish-red streaked variety, known as 'mahogany-obsidian,' has been employed to a limited extent as a decorative material in the United States. On Obsidian Cliff, Yellowstone National Park, *v.* J. P. Iddings, Seventh Ann. Rep. U.S. Geol. Survey, 1888. L. J. S.

OCCLUSION (*occludo*, to enclose). Graham's term for the process of absorption or condensation of gases within the pores of a substance, *e.g.* the absorption of hydrogen by platinum and palladium, or the condensation of marsh-gas or fire-damp in coal.

OCHRE. A name applied to various native pigments, distinguished according to colour as yellow, brown, and red ochres, and consisting essentially of ferric hydroxides (represented by the mineral species limonite and turite), usually more or less earthy by admixture with clay, or sand. When containing much manganese they pass into umber (*q.v.*). Deposits of fine yellow ochre occur in the Lower Greensand of Shotover Hill, near Oxford. Red and brown ochres are commonly associated with iron-ores, especially with the hæmatite occurring in pockets in the Carboniferous Limestone, and have been worked in South Wales, the Forest of Dean, near Bristol, at Brixham in Devonshire, Ulverston in Lancashire, and near Workington in Cumberland. Some of the finest ochres of commerce are obtained from France, and are known as Auxerre and Rochelle ochres. In the United States, ochres are worked in connection with many deposits of iron-ore, especially in Virginia and Pennsylvania. Ochre is deposited by the water of chalybeate springs and by the waters issuing from mines; in some cases such material is collected. Red ochre is formed as a by-product in the roasting of iron-pyrites. Some ochres are so pure as to be ready for use after having been simply dried, ground, and bolted; while others require careful preparation by washing and levigating. Sometimes the material is roasted to obtain the required shade of deep brown or red. The value of an ochre depends, not only on its colour, but on the proportion of oil required to be mixed with it for use as a pigment. The presence of finely-divided silica is not always detrimental to an ochre, inasmuch as it may enable the paint to adhere to fibres of the wood to which it is applied, and by filling up spaces may improve its covering power. Coarse ochre is extensively employed in the manufacture of oilcloth and linoleum, while the finer kinds of ochre are valued by the paper-maker for staining the pulp to its required tint, being especially used in the manufacture of brown paper. In commerce the term 'ochre' is frequently restricted to the pale yellowish-brown varieties. In mineralogy, on the contrary, it is extended to a variety of metallic oxides and other compounds formed as products of alteration and occurring as earthy incrustations on the minerals from which they have been derived by atmospheric action. Thus the mineralogist recognises such bodies as antimony-ochre, bismuth-ochre, molybdic-ochre, nickel-ochre (an arseniate), uranium-ochre (a sulphate), and wolfram-ochre.

References.—G. P. Merrill, The Non-Metallic Minerals, 2nd ed. 1910; T. L. Watson, Ochre Deposits of Georgia, Bull. Georgia Geol. Survey, 1906, No. 13; J. M. Hill, Mineral Paints (with Bibliography), Min. Res. U.S Geol. Survey (1912), 1913, 2, 961. L. J. S.

OCHROITE *v.* CERIUM METALS.

OCRE DE RU. *Brown ochre v.* PIGMENTS

OCTAHEDRITE *v.* ANATASE.

cyclo-**OCTANONE** *v.* KETONES.

OCTITOL *v.* CARBOHYDRATES.

OCTOIC ACIDS. $C_8H_{16}O_2$.

1. *n. Octoic acid* or *caprylic acid*

$$CH_3[CH_2]_6COOH$$

Exists as a glyceride in butter, and in human fat, and especially in cocoa-nut oil. It is also found in cheese, among the products of the distillation of fat by superheated steam, and in many fusel oils, partly free and partly in combination with different alcohol radicles. It may be prepared by oxidising normal octyl alcohol (Zincke, Annalen, 152, 9) or by the dry distillation of oleic acid (Gottlieb, *ibid.* 57, 63). It melts at 16·5° and boils at 237·5°, sp.gr. 0·9100 at 20°/4°. Sparingly soluble in cold water: 400 parts of water at 100° dissolve 1 part of the acid; readily soluble in alcohol or ether (Zincke, *l.c.*).

2. *Dipropylacetic acid, a-propylvaleric acid* $(C_3H_7)_2CH{\cdot}COOH$, is obtained by boiling ethyl dipropylacetoacetate with potash (Burton, Amer. Chem. J. 3, 389), or by heating dipropylmalonic acid (Fürth, Monatsh. 3, 319; *v.* also method of Oberreit, Ber. 1896, 2000); b.p. 219·5°, sp.gr. 0·9215 at 0°/4°. Sparingly soluble in water.

3. Iso-*octoic acid* is obtained by the oxidation of *iso*-octylalcohol (Williams, Chem. Soc. Trans. 1879, 128), b.p. 218°–220°, sp.gr. 0·911 at 20°/4°.

4. *Octoic acid* from *iso*dibutylene

$$C(CH_3)_3CH_2{\cdot}CH(CH_3)COOH$$

formed by the oxidation of the hydrocarbon; boils at about 215° with partial decomposition (Butlerow, Annalen, 189, 72). Probably identical with *iso*-octoic acid.

5. *Ethylbutylacetic acid, a-ethylhexoic acid* $CH_3[CH_2]_3CH(C_2H_5)COOH$. Obtained by the oxidation of corresponding alcohol (Raupenstrauch, Monatsh. 8, 115). B.p. 225° (Raper, Chem. Soc. Trans. 1907, 1837).

6. *Ethylisobutylacetic acid, a-ethyl-γ-methylvaleric acid* $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(C_2H_5)COOH$. Obtained by heating ethyl*iso*butylacetoacetate with alkali and alcohol (Guye and Jeanprêtre, Bull. Soc. chim. [iii.] 13, 183), b.p. 219°–220° (729 mm.); sp.gr. 0·906 at 20°/4°.

OCTYL, *Capryl* C_8H_{17}. The eighth alcohol-radicle of the series C_nH_{2n+1}. Like other members of this series, it cannot exist in the free state; when liberated from its compounds it is converted into dioctyl $C_{16}H_{34}$, a body isomeric and perhaps identical with ceryl hydride.

The compounds of this radicle occur in petroleum, in the seeds of the common- and cow-parsnip, and in the products of the distillation of some varieties of coal.

OCTYL ALCOHOL $C_8H_{17}{\cdot}OH$. A large number of isomeric alcohols with this formula are possible, but only the following have been prepared:—

(1) **Normal octyl alcohol,** *a-hydroxy octane* $CH_3[CH_2]_7OH$, occurs in the fruit of *Heracleum Sphondylium* (Linn.), the cow-parsnip, as the acetic acid ester (Zincke, Annalen, 152, 1; Möslinger, *ibid.* 185, 26); and as the acetate and butyrate in the oil of *Heracleum villosum* (Fisch.) (Franchimont, Ber. 1871, 822). Oil expressed from the ripe fruit of *Peucedanum sativum* (Benth. and Hook.), the common parsnip, is almost pure octyl butyrate (Renesse, Annalen, 166, 80). It boils at 195·5° and has sp.gr. 0·8375 at 0° (Zander, Annalen, 224, 84).

(2) **Methyl hexyl carbinol,** *β-hydroxy octane* $CH_3[CH_2]_5CH(OH)CH_3$, b.p. 179°–179·2° at 762 mm. (Schiff, *ibid.* 220, 103), 177·6°–177·8° at 745·4 mm. (Brühl, *ibid.* 203, 28); sp.gr. 0·8193 at 20°/4° (Bruhl). Heat of combustion 1,262,105 cal. (Lugunin, Ann. Chim. [v.] 25, 141).

It is formed by the distillation of alkaline ricinoleates with excess of potash (Moschnin, Annalen, 87, 111; Bouis, *l.c.*; Städeler, J. 1857, 358; Dachauer, Annalen, 106, 269; Schorlemmer, *ibid.* 147, 222). By the distillation of the saponified oil of the seed of *Jatropha curcas* (Linn.) (Silva, Zeitsch. Chem. 1869, 185).

It is a limpid, oily, inactive liquid, with a strong aromatic odour, soluble in alcohol, ether, wood-spirit, and acetic acid; insoluble in water. It dissolves phosphorus, sulphur, iodine, fused zinc chloride, fats, resins, and copals.

Preparation.—Castor oil (which contains sodium ricinoleate) is distilled with excess of potash; the portion which passes over between 176°–180° is collected and purified by fractional distillation.

On oxidation it yields, first, methyl-hexyl ketone $MeCOC_6H_{13}$; subsequently acetic and normal caproic acids are formed. It reduces silver oxide (but not nitrate) when heated with it, forming a metallic mirror. With hydrochloric acid, phosphorus pentachloride, bromine or iodine and phosphorus, &c., it exhibits the usual reactions of secondary alcohols. The ketone $C_6H_{11}Cl_2{\cdot}CO{\cdot}CCl_3$ is produced on saturation with chlorine (A. Brochet, Bull. Soc. chim. [iii.] 13, 120).

(3) **Methyl** *iso***hexyl carbinol,** *β-hydroxy-ζ-methyl heptane* $CH_3{\cdot}CH(OH)[CH_2]_3CH(CH_3)_2$ is produced by the reduction of methyl *iso*hexyl ketone $CH_3{\cdot}CO[CH_2]_3CH(CH_3)_2$ (Welt, Ann. Chim. [vii.] 6, 135). It boils at 167°–169°, and has a sp.gr. 0·8174 at 21°. It is optically active $[\alpha]_{\mathrm{D}}^{24^\circ}=4{\cdot}69^\circ$.

(4) **Methyl dipropyl carbinol,** *δ-hydroxy-δ methyl heptane* $CH_3{\cdot}C(C_3H_7)_2OH$, has been prepared by Gortaloff and Saytzeff by the action of 262 grams methyl iodide and excess of zinc on 70 grams butylene (J. pr. Chem. [ii.] 33, 204). It is a liquid boiling at 161·5°, and of sp.gr. 0·82479 at 20°. On oxidation with chromic acid it yields chiefly acetic and propionic acids.

(5) *γ*-**Hydroxy**-*δ*-**ethyl hexane**

$$(C_2H_5)_2CH{\cdot}CH(OH)C_2H_5$$

may be prepared from bromoacetyl bromide and zinc ethyl (Winogradow, Annalen, 191, 140). It boils at 164°–166°, and on warming with hydrogen iodide yields the iodide.

(6) **Diethylpropylcarbinol,** *δ-hydroxy-δ-ethyl hexane* $(C_2H_5)_2C(C_3H_7)OH$ is prepared from butyl chloride and zinc ethyl (Butlerow, Bull. Soc. chim. [ii.] 5, 17). The product is left for several days till it becomes viscid, it is then heated, acidified with hydrochloric acid and distilled. It has an alcoholic, camphoraceous odour, is lighter than water, in which it is slightly soluble and boils at 145°–155°. On oxidation with chromic acid it yields propionic and acetic acids.

(7) **Diethyl** *iso***propyl carbinol,** *γ-hydroxy-δ-methyl-γ-ethyl pentane* $CH(CH_3)_2C(OH)(C_2H_5)_2$ is produced together with ethyl *iso*propyl carbinol and ketone from *iso*butyryl chloride (1 mol.) and zinc ethyl (2 mols.). The reagents are mixed and allowed to stand in ice for three days and subsequently left together for five or six months, after which the mixture is treated with ice water (Grigorovitch and Pawloff, J. Russ. Phys. Chem. Soc. 23, 169). It boils at 159·5°–161° at 750 mm. and has sp.gr. 0·8463 at 0°.

(8) **Di***iso***butylhydrate** $C_8H_{17}OH$. Two alcohols of this name are known. (1) A primary alcohol of unknown constitution. It boils at 179°–180° at 765 mm. (uncorr.) remains fluid at – 17° and has sp.gr. 0·841 at 0°/4°, 0·828 at 20°/4° (Williams, Chem. Soc. Trans. 1879, 127). (2) A secondary alcohol obtained mixed with the primary and separated from it by fractionation. It boils at 160°–163°/75·5 mm. and has sp.gr. 0·820 at 15°/4°.

(9) *Iso***dibutol,** *β-hydroxy-βδδ-trimethylpentane* $(CH_3)_3C{\cdot}CH_2{\cdot}C(CH_3)_2OH$. boils at 146·5°–147·5°, and has sp.gr. 0·8417 at 0°/0°. It is a colourless viscid liquid, with a musty camphoraceous odour. It is prepared from di*iso*butylene hydriodide and silver hydroxide. On oxidation it yields acetone, trimethylacetic acid, acetic acid, and octoic acid $C_8H_{16}O_2$, and a ketone $C_7H_{14}O$ (Butlerow, Annalen, 189, 53).

(10) **Octylene hydrate** $C_8H_{17}OH$ is of uncertain constitution. The iodide results from the action of hydriodic acid on octylene. The alcohol is a clear liquid, boiling at 174°–178°, and of sp.gr. 0·811 at 0°. On oxidation acetic acid, caproic acid, and a ketone $C_8H_{16}O$ are obtained.

OCTANES, C_8H_{18}. Eighteen isomeric hydrocarbons having this formula are theoretically possible. Two of these occur in American petroleum (Mabery and Hudson, Amer. Chem. J. 1897, 19, 255), and are found in the portion boiling between 115° and 130°. *n*-Octane is found among the light oils obtained by distilling Wigan cannel coal at a low temperature (Schorlemmer, Chem. Soc. Trans. 1862, 419). Ligroin consists essentially of hydrocarbons having the formulæ C_7H_{16} and C_8H_{18} (Pelouze and Cahours, Annalen, 127, 197).

(1) *n*-**Octane,** *octyl hydride* $CH_3[CH_2]_6CH_3$, b.p. 125·6° (corr.), sp.gr. 0·71883 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 217); b.p. 125·2°/760 mm., sp.gr. 0·7068 at 15°/15°, $n_{\mathrm{D}}^{25^\circ}$ 1·3963 (Clarke, J. Amer. Chem. Soc. 1911, 33, 520; *cf.* Schorlemmer, Annalen, 161, 281). For thermal expansion, *see* Thorpe (*l.c.*), m.p. – 57·4° (De Forcrand).

Occurs in American petroleum; prepared by reducing *sec*-octyl iodide with zinc and hydrochloric acid (Schorlemmer, *ibid.* 152, 152), or *n*-octyl iodide with sodium amalgam (Zincke, *ibid.* 152, 15); by the action of sodium on *n* butyl iodide (Schorlemmer, *l.c.*); by heating sebacic acid with baryta (Riche, *ibid.* 117, 265).

Colourless liquid, having a faint ethereal smell. On warming with nitric acid (sp.gr. 1·42) mono- and dinitro-octane, acetic, succinic and oxalic acids, and carbon dioxide are obtained (Worstall, Amer. Chem. J. 1898, 20, 212).

(2) *β*-**Methylheptane,** iso-*octane*

$$CH_3[CH_2]_4CH(CH_3)_2$$

b.p. 116·0°/761 mm.; sp.gr. 0·7035 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3944. Has been synthesised by Clarke (J. Amer. Chem. Soc. 1909, 31, 107).

(3) *γ*-**Methylheptane**

$$CH_3[CH_2]_3CH(CH_3)CH_2{\cdot}CH_3$$

b.p. 117·6°/760 mm.; sp.gr. 0·7617 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·4022. Has been synthesised by Clarke (*ibid.* 558). The method of Welt (Ann. Chim. [vii.] 6, 121) does not yield a pure product.

(4) *δ*-**Methylheptane**

$$CH_3[CH_2]_2CH(CH_3)[CH_2]_2CH_3$$

b.p. 118·0°/760 mm.; sp.gr. 0·7217 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3978. Has been synthesised by Clarke (Amer. Chem. J. 1908, 39, 87).

(5) *βγ*-**Dimethylhexane**

$$CH_3[CH_2]_2CH(CH_3)CH(CH_3)_2$$

b.p. 113·9°/758 mm.; sp.gr. 0·7246 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·4075. Has been synthesised by Clarke (J. Amer. Chem. Soc. 1911, 33, 520).

(6) *βδ*-**Dimethylhexane**

$$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH(CH_3)_2$$

b.p. 110·0°/768 mm.; sp.gr. 0·7083 at 15°/15°; $n_{\mathrm{D}}^{25^\circ}$ 1·3986. Has been synthesised by Clarke (*ibid.* 1908, 30, 1144).

(7) **βε-Dimethylhexane,** *diisobutyl*

$(CH_3)_2CH[CH_2]_2CH(CH_3)_2$

b.p. 108·53° (corr), sp.gr. 0·711 at 0°/4° (Thorpe, Chem. Soc. Trans. 1880, 219); b.p. 108·25°/760 mm.; sp.gr. 0 6991 at 15°/15°, $n_D^{25°}$ 1·3930 (Clarke, J. Amer. Chem. Soc. 1909, 31, 585; *cf.* Schiff, Annalen, 220, 88).

Prepared by the action of sodium on *iso*butyl iodide (Wurtz, *ibid.* 96, 365) or on a mixture of *iso*amyl and *iso*propyl iodides (Schorlemmer, *ibid.* 144, 188; Kolbe, *ibid.* 69, 261); for other methods, *v.* Clarke, *l.c.* Colourless mobile liquid with ethereal odour and burning taste. Oxidation with chromic acid yields acetic acid and carbon dioxide.

(8) γδ-**Dimethylhexane**

$CH_3{\cdot}CH_2{\cdot}CH(CH_3)CH(CH_3)CH_2{\cdot}CH_3$

b.p. 116·5°/759 mm.; sp.gr. 0·7270 at 15°/15°; $n_D^{25°}$ 1·4038 (Clarke, J. Amer. Chem. Soc. 1911, 33, 520). Prepared by the action of sodium on β-iodobutane (Norris and Green, Amer. Chem. J. 1901, 26, 313).

(9) γ-**Ethylhexane**

$CH_3[CH_2]_2CH(C_2H_5)CH_2{\cdot}CH_3$

b.p. 118·8°–119°/766 mm.; sp.gr. 0·7175 at 15°/15°; $n_D^{25°}$ 1·3993. Has been synthesised by Clarke and Riegel (J. Amer. Chem. Soc. 1912, 34, 674), who state that it is probably one of the hydrocarbons found by Mabery and Hudson in American petroleum.

(10) ββγ-**Trimethylpentane**

$CH_3{\cdot}CH_2{\cdot}CH(CH_3)C(CH_3)_3$

b.p. 110·5°–110·8°/760 mm.; sp.gr. 0·7219 at 15°/15°; $n_D^{25°}$ 1·4164. Has been synthesised by Clarke and Jones (*ibid.* 170).

(11) β-**Methyl**-γ-**ethylpentane**

$CH_3{\cdot}CH_2{\cdot}C(C_2H_5)CH(CH_3)_2$

b.p. 114·0°/760 mm.; sp.gr. 0·7084 at 15°/15°; $n_D^{25°}$ 1·3996. Has been synthesised by Clarke (Amer. Chem. J. 1909, 39, 574).

(12) **Hexamethylethane** $C(CH_3)_3C(CH_3)_3$, a crystalline substance; m.p. 96°–97°; b.p. 105°–106°. Prepared by the action of sodium on *tertiary*-butyl iodide (Lwow, Bull. Soc. chim. [ii.] 35, 169).

n-**Octyl fluoride** $C_8H_{15}F$, prepared from octyl iodide and silver silicofluoride, is a colourless liquid, b.p. 131°–134°; D° 0·798 (Paternó and Spallino, Atti R. Accad. Lincei, 1907, [v.] 16, ii. 160). According to Swarts (Bull. Soc. Chim. Belg. 1921, 30 (ii.) 302), it boils at 142·5°/755 mm., and has a^{14} 0·8120, a^{21} 0·8036, $n_a^{14·1}$ 1·3952, $n_D^{14·1}$ 1·3970, $n_\beta^{14·1}$ 1·40175, $n_\gamma^{14·1}$ 1·43565. *Sec*-octyl fluoride boils at 139·3°. Mercury fluoride is preferable to silver fluoride for the preparation of aliphatic fluorides.

Octyl chlorides.

Normal chloride, *a-chlorooctane*

$CH_3[CH_2]_6CH_2Cl$

b.p. 179·5°–180°; sp.gr. 0·8802 at 16°, 0·87857 at 15° (Perkin, J. pr. Chem. [ii.] 31, 495).

Preparation.—By the action of hydrochloric acid gas on octyl alcohol (Zincke, Annalen, 152, 4). A limpid liquid, soluble in absolute alcohol and in ether, insoluble in water.

Secondary chlorides. (1) *β-Chlorooctane* $CH_3[CH_2]_5CHCl{\cdot}CH_3$, b.p. 175° (Bouis, Annalen, 92, 398), 170°–172° (Schorlemmer, Chem. Soc. Trans. 1876, 410), 168°–172° (Pelouze and Cahours, Annalen, 129, 91); sp.gr. 0·892 at 18° (Schorlemmer), 0·895 at 16° (Pelouze and Cahours).

Formation.—By the action of hydrogen chloride or phosphoric chloride on methylhexylcarbinol (Bouis); by the action of hydrogen chloride on octylene (Berthelot, Annalen, 104, 185); by the action of chlorine on octane (Schorlemmer; Wurtz, J 1863, 509; Pelouze and Cahours).

Properties.—A colourless liquid, with a strong smell of oranges.

Reactions.—It does not precipitate salts of silver. It is decomposed by potassium or sodium in the cold, yielding dioctyl $C_{16}H_{34}$. By repeated distillation with sodium, hydrogen is evolved and octylene C_8H_{16} is formed.

(2) The octyl chloride prepared from petroleum octane exhibits the same reactions as that obtained from the alcohol, but on treatment with concentrated acetic acid and potassium acetate, octylene and octyl acetate are formed in equal quantities, whereas the chloride from the carbinol yields three times as much octylene as octyl acetate (Schorlemmer, Annalen, 152, 152).

(3) *Diisobutyl chloride*, b.p. 165°; sp.gr. 0·8824 at 10·5° (Schorlemmer, *ibid.* 144, 190).

Tertiary chlorides. (1) *δ-Ethyl-δ-chlorohexane* $CH_3{\cdot}CH_2{\cdot}CCl(C_2H_5)CH_2{\cdot}CH_2{\cdot}CH_3$, b.p. 155°. A liquid with a peculiar, unpleasant odour. Prepared by the action of phosphoric chloride on the diethylpropylcarbinol (Butlerow, Bull. Soc. chim. [ii.] 5, 17).

(2) *Diethyl* iso*propylcarbinol chloride, β-methyl-γ-ethyl-γ-chloropentane.* From diethyl *iso*propyl carbinol and phosphorus pentachloride (Grigorovitch and Pawloff, J. Russ. Phys. Chem. Soc. 23, 169). Boils at 150°–155° with decomposition.

(3) Iso*dibutol chloride. ββδ-trimethyl-β-chloropentane* $(CH_3)_3C{\cdot}CH_2{\cdot}CCl(CH_3)_2$. Boils with decomposition at 145°–150°; sp.gr. 0·890 at 0°. It is formed by the action of fuming hydrochloric acid on di*iso*butylene at 100° (Butlerow, Annalen, 189, 51).

Octyl bromides.

(1) **Normal,** *a-bromooctane* $CH_3[CH_2]_6CH_2Br$, b.p. 198°-200°; sp.gr. 1·116 at 16°; 1·1178 at 13° (Perkin, Chem. Soc. Trans. 1896, 1237). A colourless liquid prepared by the action of bromine and phosphorus on *n*-octyl alcohol.

(2) **Secondary,** *β-bromooctane*

$CH_3[CH_2]_5CHBr{\cdot}CH_3$

b.p. 187·5°–188·5° at 741 mm.; sp.gr. 1·0989 at 22° (Lachowicz, Annalen, 220, 185).

Preparation.—By treating methylhexyl carbinol with bromine and phosphorus, or by saturating the carbinol with hydrogen bromide at 0°, and heating for a few hours to 100°.

Properties.—It is an oily liquid, resembling the chloride in smell; it is soluble in alcohol but not in water. It boils with decomposition and leaves a carbonaceous residue when distilled. It precipitates silver salts in alcoholic solution, but less readily than the iodide.

Octyl iodides.

Normal, *a-iodooctane* $CH_3[CH_2]_6CH_2I$, b.p. 220°-222°; sp.gr. 1·338 at 16° (Zincke, Annalen, 152, 1).

Preparation.—By the action of iodine and phosphorus or of hydrogen iodide on the alcohol (Möslinger, *ibid.* 185, 55). It is a colourless liquid which reddens on warming; it is soluble in absolute alcohol or in ether, but insoluble in water (Zincke).

Secondary iodides. (1) *β-iodooctane*

$$CH_3[CH_2]_5CHI{\cdot}CH_3$$

It boils with decomposition at 210° (Bouis, Ann. Chim. [iii] 44, 131); 193° (Squire, Chem. Soc. Trans. 1855, 108).

Preparation.—By the action of iodine and phosphorus on methylhexylcarbinol. It is an oily liquid with an odour of oranges, reddening on exposure to light. With sodium or potassium it behaves like the chloride When heated with mercury, mercurous iodide, octylene, and free hydrogen are formed. The alcoholic solution precipitates silver salts

(2) *Octylene hydriodide*, b p. 120°; sp.gr. 1·33 at 0°, 1·314 at 21°. An amber-yellow liquid insoluble in water; it is decomposed by light, and by the action of mercury in the cold.

Tertiary iodide. *Isodibutol iodide, βδδ-trimethyl-β-iodopentane*, $(CH_3)_3C{\cdot}CH_2{\cdot}CI(CH_3)_2$ is formed by the action of hydriodic acid on di*iso*butylene. It is decomposed by water (Butlerow, Annalen, 189, 52).

Octyl ethers. *Normal octyl ether* $(C_8H_{17})_2O$. From *iso*heptyl carbinol, b p. 280°-282°; sp.gr. 0·8050 at 17°, 0·82035 at 0°/0° (Dobriner). An oily liquid easily soluble in hot alcohol or ether. It is prepared by the action of sodium octoxide on the *iso*primary iodide (Moslinger, *ibid.* 185, 57; Dobriner, *ibid.* 243, 10).

Mixed ethers. *Methyl normal octyl ether* $CH_3{\cdot}O{\cdot}C_8H_{17}$, boils at 173°; sp.gr. 0·8014 at 0°/0° (Dobriner, *ibid.* 243, 4).

Ethyl normal octyl ether, boils at 189·2°; sp.gr. 0·8008 at 0°/0° (Dobriner, *l.c.*).

Propyl normal octyl ether, boils at 207·0°; sp.gr. 0·8039 at 0°/0° (Dobriner, *l.c.*).

Butyl normal octyl ether, boils at 225·7°; sp.gr. 0·8069 at 0°/0° (Dobriner, *l.c.*).

Amyl normal octyl ether, boils at 220°; sp.gr. 0·6080 at 20°/ (Wills, J. 1853, 509).

Heptyl normal octyl ether, boils at 278·8°; sp.gr. 0·8182 at 0°/0° (Dobriner, *l.c.*).

All are colourless, mobile liquids, soluble in alcohol and ether, but not in water, prepared by the action of iodides of the radicles on sodium octoxide (Wills).

Octyl sulphides. (1) *Primary sulphide* $(C_8H_{17})_2S$. Boils with decomposition over 210°; sp.gr. 0·8419 at 17°/17°. A faintly-yellow mobile liquid soluble in warm alcohol, and miscible with ether. It is prepared by the action of an alcoholic solution of potassium sulphide on normal octyl chloride (Möslinger, Annalen, 185, 60). Sulphuric acid forms with it a white amorphous mass probably of *octyl sulphone* $(C_8H_{17})_2SO_2$; mercuric chloride gives crystalline needles of $C_8H_{17}S{\cdot}HgCl_2$. It forms no compound with the alkyl iodides.

(2) *Secondary sulphide.* An oily liquid lighter than water and having an unpleasant smell. It is prepared by heating an alcoholic solution of sodium sulphide with secondary octyl iodide until the mixture becomes turbid, and then allowing the sulphide to separate out. It is slightly soluble in alcohol and decomposes on heating.

Methyl hexyl ketone $C_6H_{13}{\cdot}CO{\cdot}CH_3$. A liquid with an aromatic odour, b.p. 171°; sp.gr. 0·817 at 17°. It is obtained as a by-product in the preparation of the alcohol, also by the oxidation of the alcohol, and by the distillation of a mixture of calcium œnanthylate and calcium acetate (Staedler, J. pr. Chem. [i.] 72, 241). On oxidation it yields acetic and caproic acids. With the acid sulphites of the alkaline metals it forms compounds which crystallise in pearly scales.

Ethereal salts of primary octyl. The following constants have been determined by Gartenmeister (Annalen, 233, 249):—

	B p °	Sp gr $\frac{0°}{0°}$	Sp gr. $\frac{Bp}{0°}$	Ratio of vol. at b p. to vol at 0°	Specific volume
Formate .	198·1	0·8929	0·7156	1·2477	220·3
Acetate .	210·0	0·8847	0·6981	1·2672	245·8
Propionate	226·4	0·8833	0·6860	1·2876	270·5
Butyrate .	242·2	0·8794	0·6751	1·3028	295·6
Valerate .	260 2	0·8784	0·6618	1·3272	322·6
Caproate .	275·2	0·8748	0·6509	1·3440	349·6
Heptoate .	290·4	0·8757	0·6419	1·3651	376·2
Octoate .	305·9	0·8755	0·6318	1·3858	404·3

These esters are all colourless liquids soluble in or miscible with alcohol and ether. The first six are prepared by the action of the silver salts of the acids on the bromides or iodides of octyl. The heptoate is prepared by the action of sulphuric and heptoic acids on octyl alcohol. The octoate is obtained as a by-product in the oxidation of octyl alcohol.

Normal octyl acetate occurs naturally in the ethereal oil of *Heracleum Sphondylium* (Linn.); it is a mobile fluid with a pleasant odour of apples and a burning spicy taste. The butyrate occurs in the oil of the seeds of *Peucedanum sativum* (Benth. and Hook.).

Octyl acetoacetic ester $C_{14}H_{26}O_3$, b.p. 280°-282° (not corr.); sp.gr. 0·9354 at 18·5°/17·5°. A clear, highly refractive liquid, obtained by the action of sodium acetoacetate on octyl iodide. It decomposes on hydrolysis into octyl acetone and octyl acetic acid (Guthzeit, Annalen, 204, 2).

Octyl benzoate $C_6H_5{\cdot}COOC_8H_{17}$, b.p. 305°-306°. A colourless liquid with a weak aromatic odour easily soluble in alcohol and ether (Zincke, *ibid.* 152, 1).

Octyl sulphuric acid is prepared from concentrated sulphuric acid and octyl alcohol. The barium salt $Ba(C_8H_{17}SO_4)_2$ forms large anhydrous nacreous plates very slightly soluble in hot water and alcohol. The potassium salt

$$KC_8H_{17}SO_4$$

forms a white soluble semi-crystalline mass with a soapy feel.

Octyl nitrite, b.p. 175°-177°; sp.gr. 0·862 at 17°. Obtained by heating octyl alcohol saturated with nitrous acid to 100° (Eichler, Ber. 12, 1887).

Octyl allophanate $NH_2CO{\cdot}NH{\cdot}COOC_8H_{17}$. Shining needles melting at 155°-160°, soluble in hot alcohol. Obtained by the action of chloroformamide on the alcohol.

Ethereal salts of secondary octyl. From methylhexylcarbinol.

Secondary octyl acetate, b.p. 193° (Bouis, Annalen, 44, 135); 191°–192° (Dachauer, *ibid.* 106, 269). A mobile liquid with a pleasant fruity odour, lighter than water, soluble in alcohol and ether, and also without change in not too concentrated sulphuric acid. It is easily saponified by potash. It is prepared (1) by the action of acetic acid or of an alkaline acetate and sulphuric acid upon the secondary alcohol; (2) by the action of silver or potassium acetate on the haloid compounds of the secondary alcohol; (3) by the action of acetyl chloride on sodium octoxide.

The *monochloroacetate* is prepared by passing hydrogen chloride into a mixture of equivalent quantities of the alcohol and monochloroacetic acid and heating for 30 hours. B.p. 234°; sp.gr. 0·9904 at 10°. It is a colourless neutral mobile oil with an ethereal odour and burning taste. It is soluble in alcohol and ether.

The *di-* and *tri-chloroacetates* are prepared in a similar manner by substituting dichloro- or trichloroacetic acid. The trichloroacetate requires less heating. The former boils at 244°, the latter at 250°. They are colourless ethereal oils, lighter than water (Gehring, Compt. rend. 104 1000).

Secondary octyl nitrate $C_8H_{17}O{\cdot}NO_2$. A liquid with a pleasant smell resembling ethyl acetate. It begins to boil at 80° but soon decomposes. It is lighter than water, is soluble in alcohol, and is prepared by the action of silver nitrate on octyl iodide in alcoholic solution (Bouis).

Secondary octyl nitrite $C_8H_{17}O\,NO$. A dark yellow mobile liquid, b.p. 165°–166°; sp.gr. 0·881 at 0°. Obtained by the action of glyceryl trinitrite on the alcohol. It is soluble in ether and chloroform, and is decomposed by acids and by alcohol (Bertoni, Chem. Zentr. 1887, 35).

Secondary octyl sulphuric acid is obtained by the action of concentrated fuming sulphuric acid on methylhexyl carbinol. It is a colourless syrupy strongly acid liquid, easily soluble in water and alcohol; the diluted acid is decomposed on boiling into secondary octylic alcohol and sulphuric acid. It dissolves iron, zinc, &c., with evolution of hydrogen, and completely neutralises the bases.

The *barium salt* forms flexible nacreous plates containing three molecules of water on separating from a hot solution, or mammillary aggregations with two molecules of water on evaporating in a vacuum. It is soluble in water and alcohol, and has at first a bitter, then a sweet taste. It turns red on standing, blackens at 100°, and decomposes without melting.

The *calcium salt* forms white laminæ with a soapy feel and bitter taste.

The *potassium salt* $KC_8H_{17}SO_4{,}\frac{1}{2}H_2O$ forms white shining plates with a greasy feel; the taste is at first bitter, then sweet. It is soluble in water and alcohol, reddens and is decomposed at 100°.

Octyl phosphoric acid is formed by digesting octyl alcohol with glacial phosphoric acid. It forms soluble salts with lead or barium (Bouis).

Octyl palmitate and **stearate** are formed by prolonged heating of the alcohol with the respective acids to 200° in sealed tubes. The palmitate melts at 8·5°, the stearate at −4·5° (Hanhart, Compt. rend. 47, 230).

Octyl carbamate is formed by the action of cyanogen chloride on the alcohol, b.p. 135° (under 20 mm. pressure). It is very soluble in alcohol, from which it separates out in colourless crystals melting at 54°–55°. At ordinary pressures it boils with decomposition at 230°–232°, with partial conversion into cyanuric acid.

Octyl thiocyanate $C_8H_{17}{\cdot}S{\cdot}CN$, b.p. 142°, is formed by the action of KCNS on the secondary iodide (Jahn, Ber. 8, 805).

Octyl thiocarbimide $C_8H_{17}{\cdot}N:CS$. A colourless liquid, b.p. 234°, formed by Hofmann's reaction from octylamine by mixing with carbon disulphide in alcoholic or ethereal solution, evaporating to dryness and adding silver nitrate, or mercuric or ferric chloride to the solution of amine salt of the resulting carbaminic acid, and distilling in steam.

Octyl thiocarbamide $C_8H_{17}{\cdot}NH{\cdot}CSNH_2$, m.p. 112·5°, formed by the action of ammonia on the preceding compound. It is soluble in alcohol and ether, and separates out from its solution in colourless laminæ (Jahn, Ber. 8, 803).

OCTYLAMINES.

Only the following have been prepared—

(1) **Primary amines.**

(*a*) **Normal octylamine**, *α-aminooctane*

$$CH_3[CH_2]_6CH_2{\cdot}NH_2$$

is prepared by heating *n*-octyl iodide with alcoholic ammonia to 100° (Renesse, Annalen, 166, 85). It is also produced by treating octyl alcohol with ammonio-zinc chloride at 280° (Merz and Gasiorowski, Ber. 1884, 629); and by reducing nitrooctane with iron filings and acetic acid (Eichler, *ibid.* 1879, 1885); and in a purer condition by decomposing octyl phthalimide with concentrated hydrochloric acid at 200° (Mugdan, Annalen, 298, 145).

It is a colourless basic oil which takes up CO_2 from the air, and boils at 175°–177°/745 mm. In contact with water it forms white crystalline needles. With bromine and potash an oily compound $C_8H_{17}NBr_2$ is formed, which is converted on boiling with soda into heptyl cyanide $C_7H_{15}CN$ (Hofmann, Ber. 1884, 1920). The *hydrochloride* $C_8H_{17}NH_2{,}HCl$ is easily soluble in water and alcohol; the *platinichloride*

$$(C_8H_{17}NH_2)_2H_2PtCl_6$$

forms yellow leaves soluble with difficulty in alcohol and water; the *picrate*

$$C_8H_{17}NH_2.C_6H_2(NO_2)_3OH$$

crystallises from alcohol in oblong tables, melting at 112°–114° (Hoogewerff and Dorp, Rec. trav. chim. 6, 387).

(*b*) **Secondary octylamine**, *β-aminooctane*, is prepared by treating secondary octyl iodide from castor oil with ammonia; or methyl hexyl carbinol with ammonio-zinc chloride at 280° (Merz and Gasiorowski, Ber. 1884, 364). It boils at 162·5° (Jahn, *ibid.* 1875, 805); 175° (Bouis, J. 1855, 526); sp.gr. 0·786. It is a colourless, bitter, very caustic inflammable liquid with an ammoniacal fishy odour. It is insoluble in water, but precipitates metallic salts and dissolves silver chloride. On heating with secondary octyl iodide, ammonium iodide, octylene, polyoctylenes and the iodide of secondary octylamine are formed (Jahn, *l.c.*). The *hydriodide* $C_8H_{20}NI$ forms large plates easily soluble in water; the *hydrochloride* $C_8H_{20}NCl$ is a very deliquescent solid which crystallises *in vacuô* in large nacreous plates; the *aurichloride* $C_8H_{20}NAuCl_4$ forms shining yellow laminæ, resembling lead iodide; the *platinichloride* $(C_8H_{20}N)_2PtCl_6$ separates from boiling solution in brilliant golden yellow scales soluble in alcohol or ether.

(2) **Secondary amines.**

(*a*) **Dinormal octylamine** $(C_8H_{17})_2NH$ is produced together with *n*-octylamine by the action of ammonia on octyl iodide (Renesse, Annalen, 166, 85); or by treating octyl alcohol with ammonio zinc chloride at 280° (Merz and Gasiorowski). It crystallises in needles, melting at 36°, and boiling at 297°–298°. It is soluble in alcohol and ether, and has a strong tallow-like odour. The *hydrochloride* forms plates soluble in alcohol; the *platinichloride*

$$(C_{16}H_{35}H\cdot HCl)_2\cdot PtCl_4$$

crystallises in small scales.

(*b*) **Di-secondary-octylamine** $(C_8H_{17})_2NH$ is prepared by heating methyl hexylcarbinol and ammonio-zinc chloride to 280° (Merz and Gasiorowski). It is an oil with an aromatic odour boiling at 260°–270°. The *hydrochloride* $C_{16}H_{36}NCl$ forms small leaves; the *platinichloride* $(C_{16}H_{35}N\cdot HCl)_2PtCl_4$ forms a brown mass; the aurichloride $C_{16}H_{35}NHAuCl_4$ crystallises from alcohol in golden yellow laminæ.

(3) **Tertiary amines.**

(*a*) **Tri-normal-octylamine** $(C_8H_{17})_3N$ is formed in moderate quantity along with the mono- and di- compounds by heating octyl alcohol with ammonio-zinc chloride to 260°–280°. When pure it forms a white crystalline mass, but is usually obtained as a nearly colourless oil of agreeable odour. It boils at 365°–367°, is readily soluble in ether and absolute alcohol, but not in water. Most of its salts are liquid: the *platinichloride* $((C_8H_{17})_3NHCl)_2PtCl_4$ forms a glutinous mass insoluble in water.

(*b*) **Tri-secondary-octylamine** $(C_8H_{17})_3N$ is obtained in the same way from methylhexyl carbinol. It is a liquid boiling at 370°. It forms an oily hydrochloride. The *platinichloride* $(C_{24}H_{51}NHCl)_2PtCl_4$ is a reddish-brown resin.

Primary octyl phosphine. B.p. 184°–187°; sp.gr. 0·8209 at 17°. A limpid, mobile, highly refractive liquid, soluble in alcohol, ether, benzene, and glacial acetic acid. It is obtained by the action of phosphonium iodide and zinc oxide upon normal octyl iodide at 170° (Moslinger, Annalen, 185, 65).

Nitric acid oxidises the solution in glacial acetic acid to *octylphosphinic acid*, an amorphous compound soluble in hot acetic acid. Oxygen, bromine, and iodine act less energetically upon octyl phosphine than upon the phosphines of the lower members of the series. Fuming hydriodic acid forms *octyl phosphonium iodide* $PH_3C_8H_{17}I$, a semi-crystalline mass which decomposes on standing, or on solution in ether or benzene.

Octonitrile, ***heptyl cyanide*** $C_7H_{15}CN$, boils at 194°–195°; sp.gr. 0·8201 at 13·3° (Felletar, J. 1868, 634); b.p. 198°–200° (Hofmann, Ber. 1884, 1410).

n*-Octyl cyanide,** ***pelargonic nitrile, boils at 214°–216°; sp.gr. 0·786 at 16°/4° (Hell and Kitrosky, *ibid.* 1891, 985; Eichler, *ibid.* 1879, 1888).

Octoamide, *caprylamide* $C_7H_{15}CO\cdot NH_2$, crystallises in leaves melting at 97°–98° (Aschan, Ber. 1898, 2348), 110° (Felletar, J. 1868, 624). It is prepared by dropping the acid chloride into ammonia (Aschan, *l.c.*), or by heating ammonium octoate (Hofmann, Ber. 1882, 983). It is very slightly soluble in boiling water, and not at all in cold.

Nitro-octane. A liquid boiling at 205°–212°, obtained together with octyl nitrite by the action of silver nitrite on primary octyl iodide (Meyer, Annalen, 171, 23; Eichler, Ber. 1879, 1883).

Octyl nitrolic acid $C_8H_{16}NO\cdot NO_2$. An oily body formed from nitro-octane by saturating its solution in 10 volumes of water with nitrous fumes Concentrated sulphuric acid decomposed it into octoic acid and nitrous oxide (Eichler, Ber. 12, 1885).

BENZENE DERIVATIVES OF PRIMARY OCTYL.

Octylbenzene $C_6H_5\cdot C_8H_{17}$. A colourless oil with a sweet taste, b.p. 261°–263° (uncorr.); sp.gr. 0·849 at 15°/15°; b.p. 262°–264°: sp.gr. 0·852 at 14° (Ahrens, Ber. 1886, 2717) (Schweinitz, *ibid.* 640). It is obtained by the action of sodium on a mixture of bromobenzene and normal octyl bromide in ethereal solution; or from bromobenzene, normal octyl iodide and sodium (Lepinski, Ber. 1898, 938). It is miscible with alcohol, ether, or benzene.

Chloro-octylbenzene $C_6H_4ClC_8H_{17}$ is a yellowish odourless oil soluble in alcohol and ether, b.p. 270°–275°. It is prepared by the action of chlorine and iodine on octylbenzene (Ahrens, Ber. 1886, 2719)

Bromo-octylbenzene $C_8H_{17}\cdot C_6H_4Br$, b.p. 285°–287°, resembles the chloro derivative, and is prepared by warming octyl benzene with bromine water (Schweinitz, Ber. 1886, 642).

p-**Iodo-octylbenzene.** A heavy oil, b.p. 318°–320°, prepared from *p*-amino-octylbenzene (*q.v.*) by the diazo- reaction (Beran, Ber. 1885, 136). By treating octylbenzene, diluted with petroleum, with iodine and mercuric oxide, a yellow oil is obtained, which is probably identical with the preceding compound.

The corresponding derivative of the secondary alcohol (from castor oil) is a yellow oily liquid, b.p. 304°–305°. On oxidation with chromic acid both yield *p*-iodobenzoic acid.

m-**Nitro-octylbenzene** $NO_2\cdot C_6H_4\cdot C_8H_{17}$. Crystallises in long needles which melt at 123°–124° and sublime at a high temperature. It is prepared by the action of fuming nitric acid upon octylbenzene in the cold. It is slightly soluble in alcohol and chloroform. With potassium permanganate it yields *m*-nitrobenzoic acid (Ahrens, Ber. 1886, 2725).

o-**Nitro-octylbenzene** is a thick yellow aromatic oil which decomposes at 100°. It is prepared by treating octylbenzene with fuming nitric acid and warming after filtering off the precipitated crystals of *m*-nitro-octyl benzene (Ahrens, *l.c.*).

p-**Nitro octylbenzene** which forms small yellow lustrous needles melting at 204°, and soluble in alcohol or ether, is found in the residue from the meta- and ortho- compounds (Ahrens, *l.c.*).

Dinitro-octylbenzene $C_8H_{17}\cdot C_6H_3(NO_2)_3$ forms crystals melting at 226°, but subliming below this temperature. It is soluble in alcohol and ether and is formed by the action of fuming nitric acid on the crystals of the meta- compound (Ahrens).

o-**Amino-octylbenzene hydrochloride**

$$C_8H_7\cdot C_6H_4\cdot NH_2,HCl$$

occurs in small lustrous white plates which redden on heating. It is formed by reducing the nitro derivative with tin and hydrochloric acid (Ahrens, Ber. 1886, 2717).

p-**Amino-octylbenzene,** a colourless liquid, b.p. 310°–311, volatilises in steam. It is obtained by the action of aniline hydrochloride, or of aniline and zinc chloride on primary octyl alcohol (from *Heracleum* oil). A similar derivative may be prepared from the secondary alcohol (from castor oil), b.p. 290°–2[illegible]2° (corr.) (Beran, Ber. 1885, 132).

Formylphenoctylamine, *formylamino-octylbenzene* $C_8H_{17}\cdot C_6H_4\cdot NH\cdot CHO$, is obtained by the action of formic acid on *p*-aminoctylbenzene. It forms scales which melt at 56° and are soluble in alcohol or ether (Beran, Ber. 1885, 135).

Acetylphenoctylamine, *acetylamino-octylbenzene* $C_8H_{17}\cdot C_6H_4NH\cdot C_2H_3O$, is formed from *p*-amino-octylbenzene and acetic anhydride. It forms thin plates melting at 93°, and soluble in alcohol or ether (Beran).

Benzolphenoctylamine, *benzoylamino-octylbenzene* $C_8H_{17}\cdot C_6H_4NHBz$, is obtained from *p*-amino-octylbenzene and benzoyl chloride. It forms scales melting at 117° and soluble in alcohol or ether. The corresponding derivative of the secondary alcohol forms white needles melting at 109° (Beran).

p-**Octylbenzonitrile** is obtained by distilling formylphenoctylamine with zinc-dust; b.p. 312°. It is converted by oxidation into *p*-octylbenzoic acid.

Octylbenzene sulphonic acid. A thick syrupy strongly acid liquid formed by the action of Nordhausen acid on octylbenzene. Silver salt $C_8H_{17}\cdot C_6H_4\cdot SO_3Ag,H_2O$. Barium salt

$$(C_{14}H_{21}SO_3)_2Ba,H_2O$$

Lead salt $(C_{14}H_{21}SO_3)_2Pb,3H_2O$ (Schweinitz, Ber. 1886, 640).

TOLUENE DERIVATIVES OF PRIMARY OCTYL.

Amino-octyltoluene (*Toloctylamine*)

$$C_8H_{17}C_6H_3MeNH_2$$

is prepared by treating the normal alcohol with *o*-toluidine and zinc chloride. It is a colourless oil which boils at 324°–326°, and forms a well-crystallised hydrochloride, sulphate, and oxalate (Beran, Ber. 1885, 146).

Acetyltoloctylamine $C_8H_{17}\cdot C_7H_6\cdot NHAc$ forms slender white needles, m.p. 81°, soluble in alcohol and ether (Beran, *l.c.*).

Benzoyltoloctylamine $C_8H_{17}\cdot C_7H_6\cdot NHBz$ forms lustrous scales, m.p. 117°, soluble in alcohol. These toluene derivatives are prepared in a manner analogous to the corresponding benzene derivatives (Beran, *l.c.*).

THIOPHEN DERIVATIVES OF PRIMARY OCTYL.

(Schweinitz, Ber. 1886, 644 *et seq.*)

Octylthiophen $C_8H_{17}\cdot C_4H_3S$ is formed by the action of sodium on octyl bromide and iodothiophen, b.p. 257°–259°; sp.gr. 0·8181 at 20·5°/20·5°. It is soluble in ether.

Bromo-octylthiophen $C_4SH_2Br\cdot C_8H_{17}$ boils at 285°–290° and solidifies at 5°.

Iodo-octylthiophen $C_4SHI\cdot C_8H_{17}$ is a yellow oil which solidifies at 0°; sp.gr. 1·2614 at 20°/20°. Both the bromo and iodo compounds are prepared analogously to the corresponding benzene derivatives.

Octylacetothienone $C_8H_{17}\cdot C_4SH_2\cdot COMe$, an oil with a garlic-like odour, b.p. 350°–355°, and **Octyldiacetothienone** $C_8H_{17}\cdot C_4SH(COMe)_2$, a yellow syrup, are prepared by the action of acetyl chloride and aluminium chloride on octylthiophen.

Octylthiophen-di-carboxylic acid

$$C_8H_{17}\cdot C_4SH(COOH)_2$$

is obtained in microscopic needles melting at 185°, by the action of potassium permanganate on the mono and diacetyl derivatives. Barium, copper, and silver salts have been prepared.

ββ-**Methyloctylthiophen** $C_8H_{17}\cdot C_4SH_2Me$ is obtained by the action of sodium on *ββ*-methyl iodothiophen and octyl bromide. It is a colourless oil boiling at 270°–275°, and on strongly cooling it solidifies to a crystalline mass which melts at 10°. The monobromo derivative $C_8H_{17}C_4SHMeBr$ melts at 20°.

OCUBA WAX *v.* WAX.

ODONTOLITE *v.* TORQUOISE.

ODORINE. A volatile base found by Unverdorben in bone-oil. Probably impure picoline.

ODOUR AND CHEMICAL CONSTITUTION.

The means at our disposal for measuring odour are so unsatisfactory that great difficulty confronts the investigator of the relations between odour and chemical constitution. Colours can be investigated by the spectroscope and resolved into components of known wave lengths bearing a definite relationship to each other, and our knowledge of the relation of the colour of a substance to its chemical constitution has been greatly advanced by the study of absorption spectra in the infra-red and ultra-violet regions. At present we are without knowledge as to the physical basis on which odour depends, and observers are not even agreed as to the most probable conjecture; we know of no instrument which is affected by the odour of a substance, and we cannot record smells or trace relationships between them.

In order that an odoriferous substance may be detected by the nose, it is essential that the substance should be volatile. Although the conditions which produce odour and volatility are frequently the same, it is possible to have a volatile substance, such as water, entirely without smell, so that it is clear that the conditions which produce odour and volatility are not identical. Since ammonia, with a molecular weight less than that of water, is odorous, the lack of odour in water cannot be explained by assuming that the molecular weight of water is below a limiting value necessary to produce odour; the nasal nerve endings being soaked in water are probably unaffected by it It is possible that a substance, apparently odourless, might possess a chemical constitution which would condition odour if the substance could be obtained in a volatile state at a temperature suitable for examination. The limits of sensitiveness of odours and emanations were investigated by Berthelot, who found that the odour of iodoform is detectable when 1 gram of the substance loses $\frac{1}{10^{12}}$ gram per hour; in one hundred years the loss from 1 gram under the conditions of the experiment would be less than 1 mg., and with musk the loss of weight associated with the perception of odour is 1000 times less (Compt. rend. 1904, 1249).

Two properties of odours may be recognised, intensity and quality, of which intensity alone lends itself to quantitative measurement. Various olfactometers have been described (*cf.* Van Dam, Arch. Neerland Physiol. 1917, 660), which compare the intensity of odours by determining the dilution at which the odour is perceptible. The quality of a smell may be profoundly influenced by dilution, a substance which in concentrated form is highly objectionable, becoming exceedingly pleasant when diluted. The odour of a substance is also greatly changed by the presence of impurities.

The solubility of an odoriferous substance has been described as of importance. Backman (J. physiol. path. gen. 1917, 1) contends that for a substance to be odorous it must not only be volatile but it must be soluble in water and in lipins, in order that it may come into contact with the cells of the receptor organ for smell, which are covered with a watery fluid containing lipin granules. Kremer (Arch. Neerland Physiol. 1917, 715), using a spectroscopic method, has shown that when air saturated with an odoriferous substance, *e.g.* pyridine or camphor, is bubbled through a suspension of lipin in water, more odoriferous substance is absorbed than when the saturated air passes through water alone. Odour seems to vary independently of such physical properties as colour, refraction, and specific gravity. The molecular weights of odoriferous substances lie between 17 and 300 (Zwaardemaker, Arch. Neerland Physiol. 1922, 336), but within these limits no connection between the odour and the molecular weight has been satisfactorily established. Indeed, the fact that substances of the same molecular weight have quite different odours, *e.g.* vanillin and citral, would appear to show that the effect on smell must be looked for in some property other than the weight of the molecule. It is true that as we ascend a homologous series we reach a maximum intensity of odour which then diminishes as we ascend the series, but the maximum is reached at quite different molecular weights in the different series of compounds. Durrans gives an interesting table, showing the influence of the molecular weight in certain groups of compounds (Perfumery Record, May, 1919):

In aliphatic saturated	Odour develops at	Reaches a maximum at	Is lost at
Alcohols . .	C_5	C_8	C_{14}
Aldehydes . .	C_1	C_{10}	C_{16}
Ketones . .	C_8	C_{11}	C_{16}
Acids . .	C_1	C_5	C_{14}
Esters . .	C_6	C_8	C_{17}

No direct connection between odour and any one physical property has yet been satisfactorily established, though much interesting work has been done, and valuable suggestions have been made. Tiemann observed that optically active compounds had a more intense odour than their racemic isomerides (Ber. 28, 2117). Tyndall suggested that there was a connection between intensity of odour and the power of absorbing radiant heat, but Grijns (Arch. Neerland Physiol. 1919, 37) failed to detect any such relationship, and concluded that the olfactory apparatus was not affected by the liberation of energy absorbed from radiant heat. Durand (Compt. rend. 1918, 129) suggested that smell is caused by the retention in the nose of odorant ions; in support of this view he urged that both musk and camphor greatly increase the condensing power of dust-free air for aqueous vapour. The relation of electrical phenomena to intensity of smell has also been studied by Zwaardemaker (Abs. Chem. Soc. 1917, ii. 62; 1920, ii. 75), who observed that positive electric charges were produced by spraying aqueous solutions of odorous substances. Using aliphatic alcohols and acids he showed that when the solutions were diluted until the electric phenomena were only just appreciable the smell also could only just be detected; both properties depended on volatility and the lowering of the surface tension of the solvent. The diamagnetic properties of odoriferous substances have also been examined by Zwaardemaker and Hogewind (Arch. Neerland Physiol. 1920, 224), who, however, failed to find any marked correlation between these two properties.

Teudt (Chem. Centr. 1919, 138), starting from the standpoint that the origin of odour must be within the molecule, attributed its cause to the vibrations of the valency electrons. He pointed out that whereas the molecule of chlorine is intensely odorous, the chlorine ion does not produce odour, in the chlorides for instance, and he suggested that the electron vibrations of the nasal sensory nerves were increased by resonance when odoriferous particles having corresponding intra-molecular electron vibrations were drawn into the nose mixed with air. A similar theory has been put forward by Kodama (J. Tokyo Chem. Soc. 1920, 975; *cf.* Ungerer and Stoddard, Ungerer's Bull. 1922, 3, 7). Teudt's theory has been adversely criticised by Heller (American Perfumer, 1920, 365), and by others.

In all these attempts to correlate both the physical properties and the chemical structure with this property of odour, we are met with the difficulty of comparing different classes of odour; the unsatisfactory nature of our standard of comparison of odours is apparent from the descriptions used in designating the members of any series of compounds. The terms lemon-like, flower-like, camphor-like, musk-like, and so forth are used; there are a certain number of well-defined odours to which we refer as far as we can, but we are without knowledge of any relation between these various characteristic odours. It is true that as early as 1865, Piesse (Des Odeurs des Parfums et des Cosmetiques) arranged all known perfumes in order of volatility, and produced a scale of six and a half octaves from patchouli to civet (Perfumery Record, 1919, 268). Later Linné introduced a classification of odours which has been somewhat modified by Zwaardemaker (*l.c.*), who claims that the classes of odour differentiated by modern work on the rapidity with which fatigue is induced coincide with some of the sub-classes of this classification. Nine classes are here recognised: (1) ethereal odours; (2) aromatic odours, which powerfully excite olfactory sensations but do not produce much fatigue and are rapidly lost by evaporation—these are subdivided into (*a*) camphoraceous odours, *e.g.* eucalyptol and camphor; (*b*) almond odours, *e.g.* benzaldehyde, nitrobenzene, and acetophenone; (*c*) citral odours, including citral and the cyclic limonene; (3) floral or fragrant odours—these can be greatly diluted while still continuing to excite olfactory sensation but easily induce fatigue; (4) ambrosiac odours, *e.g.* musk; (5) allyl and cacodyl odours; (6) empyreumatic odours, containing the benzene hydrocarbons from benzene to durene; (7) hircin odours, including the fatty acid series; (8) repulsive odours (Linné), such as pyridine and quinoline; (9) fœtid odours, such as indol and skatol. The differentiation between the various classes is not always sharp, and members of the same homologous series with similar structures may belong to quite different classes.

Many attempts have been made to correlate the presence of odour with the possession of certain definite atomic groups. Here we are met with the anomaly that substances containing quite different groups and even of quite different structure may produce odours which are indistinguishable, *e.g.* trinitro butyltoluene (artificial musk), and the ketone, muskone which forms the characteristic constituent of natural musk; the close resemblance of the smell of benzaldehyde to that of nitrobenzene and the similarity of the odours of bornyl acetate and trichlor tertiary butyl alcohol afford other examples.

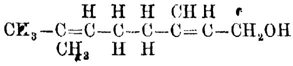
Von Liebig suggested that the odour of a substance was connected with its tendency to undergo oxidation, and claimed that those ethereal oils which were most easily oxidised had most smell. Woker (J. Physikal. Chem. 1906, 455) accepted the view that volatility and odour were produced by the same conditions and resulted from a state of strain within the molecule. Other conditions being the same, the intensity of odour increased as the degree of saturation diminished. Thus a triple linking produced a more marked effect than a double bond, and generally the effect was intensified by increasing the number of double bonds in the molecule. Woker laid stress on the importance of the unsaturated linkages, and attributed both volatility and odour to the intramolecular tension, and considered that both increased with an increase in the intramolecular repulsive forces. The introduction of similarly charged groups into the molecule would increase the repulsive forces, but groups with charges of opposite signs would diminish both volatility and odour. Volatility is markedly increased by loading a carbon atom with identical groups, and at the same time the camphoraceous odour of the tertiary carbon compounds results.

Klimont (Die synthetischen und isolirten Aromatica, 1899) limited his survey to ‘aromatic’ substances having a pleasant odour, and connected with this property the presence of certain groups which he designated as ‘aromatophors.’ These comprised the groups characteristic of alcohol, aldehyde, ketone, carboxyl, carboxyl ester, lactone, phenol, nitro and thiocyanide compounds, with certain nitrogen-containing radicles. He regarded both quality and intensity of aroma as depending on these groups, which varied greatly in the effect they produced. Thus the feebly smelling pyrocatechin $1.2.C_6H_4(OH)_2$ when one OH group is replaced by a methoxy group is converted to the aromatic guaiacol, and this in turn is converted by the introduction of the potent aldehyde group to the intensely smelling vanillin

$$1.3.4.C_6H_3{\cdot}OH{\cdot}OCH_3.CHO$$

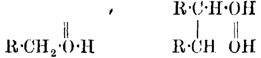
it has been noted that the 1.3.4. positions in the benzene ring are particularly favourable for the development of smell. Again, the replacement of the group $\begin{matrix}-O\\-O\end{matrix}\!\!>\!CH_2$ by the groups $-OH$ and $-OCH_3$ is seen in the change from safrol to the intense carnation odour of eugenol. Klimont drew attention to the importance of the double bond and of its position in the molecule and to the much less pleasant effect of the triple bond, and pointed out that in a homologous series to some extent the intensity of the smell was a function of the boiling-point, but that marked changes in the quality of the smell also occurred, *e.g.* aldehydes and acids both produce unpleasant acrid odours in the lower members of the series, mildly aromatic odours in the higher members. Similar ideas have been expressed by other writers; the term ‘odoriphor’ was suggested by Zwaardemaker, and ‘osmophoric group’ was introduced by Rupe and Majewski (Ber. 1900, 3401), these groups being similar to the aromatophors of Klimont; they comprised the groups $-OH$, $=O$, $-COMe$, $-OMe$, $-CHO$, $-NO_2$, $-CN$, $-N_3$ (triazo), the last-named four groups being very similar in their effects and producing similar odours in analogously constituted substances; instances of this are seen in the similarity of benzaldehyde, nitrobenzene, and cyanobenzene, and of vanillin *p*-nitroguaiacol, and *p*-cyanoguaiacol.

Cohn introduced two new terms—‘enosmophor’ for a group producing a pleasant odour, and ‘kakosmophor’ for a group producing a disagreeable odour—but this differentiation does not seem helpful. Marchand (Deutsch. Parfum. Ztg. 1915, 232), differentiated between the class of odour and its shade or tinge, and regarded the former as determined by the non-osmophoric part of the molecule, the latter by the osmophoric group. Prins (Perfumery Record, 1917, 222) preferred to regard all groups as osmophoric, but differing in strength. It is obvious that the benzene nucleus confers a certain similarity of smell on its derivatives which the substituting osmophoric group does not entirely overcome; the aliphatic hydrocarbon chain exerts a comparatively slight influence, so that the entering osmophor has more effect, and the odours of the alcohol, aldehyde, and acid in the fatty series are more strongly differentiated than in the benzene series. Comparisons of the odours of certain closely related substances have been carried out by various observers, such work being of importance from the point of view of synthetic perfumes, where a slight modification in the constitution of a compound may produce a useful difference in odour, as well as from the theoretical standpoint of the relation of odour to constitution. As an instance, the work of Austerweil and Cochin (Compt. rend. 150, 1693; 151, 440) on geranic and rose odours may be quoted. Geraniol is represented by the formula:

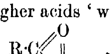


$$\mathrm{CH_3{-}\underset{CH_3}{C}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\overset{CH}{C}{=}\overset{H}{C}{-}CH_2OH}$$

Substitution of either one or two of the hydrogen atoms of the alcohol radicle by the methyl and ethyl groups give compounds very similar in odour to the original compound. With the introduction of the isobutyl or phenyl radicle the smell is less intense, and in the latter case becomes somewhat rose-like in character. Closing the ring produces a marked effect, for in methyl cyclogeraniol the odour almost disappears. Reduction of the $\alpha\beta$ double bond changes the character of the smell, giving a more rose-like odour. Substitution of one or two hydrogen atoms of the alcohol group by the methyl or ethyl groups has here also little effect upon the odour; this becomes less distinct in the propyl and butyl compounds, but the rose odour is intensified by the introduction of the phenyl group. A systematic review of odorous compounds was made by Durrans (Perfum. Record, May 1919), who regarded as unsatisfactory the suggestion that all groups are osmophoric; he considered the possession of residual valency as the essential attribute of the osmophor. In hydrocarbons, for instance, the benzene nucleus exerts much more influence on odour than the fatty hydrocarbon radicle; the addition of two hydrogen atoms to the ring greatly increases the odour which diminishes with the successive addition of two pairs of hydrogen atoms. Thus the most unstable condition is associated with the most marked odour. The failure of the presence of two osmophors in glycol to produce odour is explained by representing the oxygen atoms of glycol with bound valencies as expressed in the following formulæ:



Alcohol Glycol

It is difficult, however, to accept the suggestion that oxygen in the esters and lower acids should be represented as in the formula $\mathrm{RC}\!\left\langle{}^{\mathrm{O}}_{\mathrm{OH}}\right.$ and in the higher acids 'where R is large' as in the formula , a formula suggested on other grounds for the carboxyl group (*cf.* Smedley, Trans. Chem. Soc. 1909, 231). It seems unnecessary to introduce a different formula for the higher and lower fatty acids when increase of molecular weight leads to loss of smell in every series of compounds, as Durrans clearly pointed out. The view that the stimulus of the olfactory nerve endings is brought about by some kind of chemical combination between the odoriferous substance and the substance of the nerve ending has found considerable support (*cf.* Durrans, *l.c.*; Tschirch, Abs. J. Chem. Soc., 1921, i. 755), and is founded on the importance of the residual valencies in conditioning odour. Such a method would certainly present a wide divergence from what we know as to the means of stimulation of the other sense organs.

The main conclusions from the above statement of the present position of the subject are: (1) It is clear that in order to be odorous a substance must be volatile, and that a sufficient rise in molecular weight diminishes the volatility, and when a sufficiently high molecular weight is reached the odour is lost. (2) Groups of atoms vary much in the effect they produce when introduced into a compound, but many groups have a recognisable and characteristic effect. Groups with residual valencies are most potent in their effect; essentially different groups of atoms may, however, produce odours which closely resemble one another. The position of the double bond in the molecule and the position of the substituents in the benzene ring exercise a great effect on odour. (3) At present all attempts to regard odours as produced by the summation of the properties of a series of groups of atoms have been unsuccessful, and it is permissible to draw the conclusion that it is to some property of the whole molecule we must look for its cause. Whether the theory of Teudt is correct, that it is the vibrations of the valency electrons in the molecule which cause smell or whether some other hypothesis will prove more fruitful, the osmophoric groups appear to act through their influence on the whole molecular structure, and the whole molecule appears to be concerned in providing the stimulus of the olfactory organ.

Cf. Delange (Bull. Soc. Chim. 1922, [iv.] 33, 589), who gives an extensive bibliography on the subject. I. S. M.

iso-**ŒNANTHIC ACID** *v.* HEPTOIC ACIDS.

ŒNANTHIC ACID *v.* HEPTOIC ACIDS.

ŒNANTHIC ETHER. According to Liebig and Pelouze (Annalen, 19, 241), there is found in wine a small quantity of a body termed by them œnanthic ether. It is a very mobile liquid, with a strong vinous smell, and of a disagreeable taste; readily soluble in ether and alcohol, but very sparingly soluble in water. This ether is now prepared commercially for flavouring common wines, brandy, &c., from the oxidised products of oil of rue. According to A. Fischer (Annalen, 115, 247) the artificial product is a mixture of capric and caprylic acids. Many fusel oils contain both these acids, and amyl caprate is found in several Hungarian wines.

ŒNANTHOL, *œnanthaldehyde, heptaldehyde, normal œnanthic or heptoic aldehyde,* $C_6H_{13}CHO$, is one of the products of the dry distillation of alkaline ricinoleates and of the action of nitric acid on stearic and margaric acids. It is also formed when fats and oils turn rancid (Scala, Chem. Zentr. 1898, i. 439).

The following method of preparation may be employed:—

Castor oil, which consists essentially of the glyceride of ricinoleic acid, is rapidly distilled until the residue becomes resinous, thus converting the greater part of the ricinoleic acid into œnanthol and hendecatoic acid:—

$$C_{18}H_{34}O_3=C_6H_{13}CHO+C_{11}H_{20}O_2$$

The distillate is rectified, and the part coming over between 90° and 180° is shaken with a saturated solution of acid sodium sulphite, and is warmed and filtered. The mass of the double salt $C_8H_{13}CHO{\cdot}HNaSO_3,H_2O$, separating out on cooling, is pressed between filter paper, mixed with a solution of sodium carbonate, and distilled in a current of steam. The œnanthol which floats on the distillate is separated and dried over anhydrous sodium sulphate or calcium chloride (Bussy, Annalen, 1846, 60, 246; Erlenmeyer and Sigel, *ibid.* 1875, 176, 342).

The yield of œnanthol is increased when the castor oil is distilled under reduced pressure (Krafft, Ber. 1877, 10, 2035; Jourdan, Annalen, 1880, 200, 102).

A better yield is obtained by distilling the ethyl or preferably the methyl ester of ricinoleic acid at ordinary pressure. The distillate is redistilled, treated with sodium bisulphite and the crystalline mass thus obtained is washed with ether and well drained. The œnanthol can then be isolated in the ordinary way (Haller, Compt. rend. 1907, 144, 462).

Œnanthol is also prepared by the following process: Castor oil or rape oil is heated in an iron boiler to 160°, and air is blown through, the source of heat is then removed and the temperature of the mass rises spontaneously to 220°. The vapours are condensed and the oily layer is treated with sodium bisulphite. The œnanthol is then separated as above (D. R. P. 167137; Frdl. 1905–07, 40).

Œnanthol reacts with diazoacetic ester yielding non-crystalline ethyl œnanthylidene-1:2-dioxynonylate, b.p. 200°/14 mm. On saponification the latter yields an acid which on boiling with acetic acid decomposes with formation of œnanthol (Dieckmann, Ber. 1910, 43, 1027).

Œnanthol is a highly refractive, very mobile, colourless liquid, of pungent aromatic smell, boiling at 154° at 747 mm. pressure, and having at 15° a sp.gr. of 0·8231 (Perkin, jun., Ber. 1882, 15, 2802; D. R. P. 126736, 1902), b.p. 152·2°–153·2° (corr.) sp.gr. 0·82264 at 15° (Perkin, Chem. Soc. Trans. 1884, 476), b.p. 42°–43°/10 mm., sp gr. 0·8250 at 20° (Semmler, Ber. 1909, 42, 1161; Harries and Oppenheim, Chem. Zentr. 1916, ii. 991). It is slightly soluble in water, and dissolves in all proportions in alcohol and ether. Œnanthol rapidly oxidises on exposure to air. It reduces silver nitrate. It forms a mono- and a dihydrate (Noorduyn, Rec. trav. chim. 1919, 38, 345).

When heated at 190° in sulphuric acid, it blackens, and a small quantity of carbon monoxide and much sulphur dioxide are evolved (Bistrzycki and Fellmann, Ber. 1910, 43, 776).

Reduction by sodium amalgam in acetic acid solution yields *n*-heptyl alcohol, b.p. 90°/14 mm. If an excess of sodium is avoided and the solution is not kept acid diheptylenealdehyde is produced:

$$CH_3{\cdot}[CH_2]_5{\cdot}CH : C(CHO){\cdot}[CH_2]_4{\cdot}CH_3$$

D^{20} 0·8463 (*cf.* Perkin, Chem. Soc. Trans. 1883, 43, 67; Levene and Taylor, J. Biol. Chem. 1918, 35, 281).

With nitric acid, œnanthol yields dinitrohexane, hydroxylamine and heptoic acid (Ponzio, J. pr. Chem. 1895, [ii.] 53, 431). Œnanthol reacts with cyanacetic acid in the presence of piperidine forming αγ-dicyano-β-hexyl-glutaric acid, m.p. 442° (D. R. P. 156560; Frdl. 1902–04, 738; *see* also Guareschi, Chem. Zentr. 1903, ii. 193; Annalen, 1903, 325, 205). It also reacts with malonic acid forming Δ′ nonylenic acid (D. R. P. 156560; Harding and Weizmann, Chem. Soc. Trans. 1910, 299).

Œnanthol condenses with aniline (Miller, Ber. 1892, 25, 2020); with aniline sulphite (Eibner, Chem. Zentr. 1901, i. 1360; Speroni, Annalen, 1902, 325, 354); with acetone (Rupe and Hinterlach, Ber. 1907, 40, 4764); with oxalacetic ester in presence of ammonia (Simon and Conduché, Ann. Chim. 1907, [viii.] 12, 5); and with hydrazobenzene (Russow, J. pr. Chem. 1909, [ii.] 80, 511). It also reacts with a number of other substances (Fittig and Reechelmann, Annalen, 1889, 255, 126; Miller, *l.c.*; Fischer and Giebe, Ber. 1897, 30, 3054; Knoevenagel, Ber. 1898, 31, 730; Claisen, *ibid.* 1014; Neuberg and Neimann, *ibid.* 1902, 35, 2049; Lees, Chem. Soc. Proc. 1902, 213; Tschitschenko, J. Russ. Phys. Chem. Soc. 1906, 38, 482; Schlotterbeck, Ber. 1907, 40, 479; Braun, *ibid.* 1908, 41, 2169; Semmler, *l.c.*).

Œnanthaldoxime boils at 100·5°/14 mm. It only solidifies partially and the solid part melts at 55·5° (Bourgeois and Dambmann, Ber. 1893, 26, 2856). It forms a number of derivatives (Goldschmidt and Zanoli, Ber. 1892, 25, 2573; Comstock, Amer. Chem. J. 1897, 19, 485; Conduché, Ann. Chim. 1908, [viii.] 13, 5; Irvine and Moodie, Chem. Soc. Trans. 1908, 102).

ŒNANTHYLIC ACID *v.* HEPTOIC ACID.

ŒNIDIN, ŒNIN. The red pigment of the young leaves of *Vitis vinifera* is a free anthocyanidin, probably identical with œnidin, the anthocyanidin of the purple grape. The pigment may occur in a colourless modification, or leuco-anthocyanin, combined with another substance. On treatment with acids it forms anthocyanidin (Rosenheim, Biochem. J. 1920, 14, 178).

ŒNOCYANIN, the colouring matter of black grapes and red wines, is of colourless origin, and becomes blue through oxidation, and probably hydration, which may be shown by placing a green grape picked from a bunch which is just beginning to turn red in a vacuum of 1–2 mm. over boiled sulphuric acid for 3 or 4 days, or sufficient time to allow of the grape becoming hard and dry. The colour becomes yellow, but, on admitting air, moisture and oxygen are rapidly absorbed, the colour changing to blue black at the same time (Maumené, Compt. rend. 95, 924). Œnocyanin cannot be extracted from grape marcs and lees of wine, but is obtained from red wines destined for distillation by the following method: the wine is treated with sufficient basic lead acetate to precipitate the colouring matter, the precipitate is collected on a filter and washed until the filtrate contains only traces of lead (24 hours). The precipitate is weighed moist and the dry substance and lead oxide are determined in an aliquot portion. The remainder is then treated with exactly the calculated quantity of sulphuric acid and filtered hot. The colouring matter passes into the filtrate and is obtained in the form of a syrup soluble in water or alcohol by evaporating the solution to the required consistency after adding glycerol in the proportion of 10 grams of glycerol to the extract from 1 litre of wine. The solution of œnocyanin thus obtained is used for increasing the colour of poor wine and also for colouring confectionery and liqueurs. Œnocyanin is not a uniform substance and its proportion in red wines varies from 9·2 to 18·7 grams per litre (Cari Mantrand, Bull. Soc. chim. 1906, 35, 1017, 1022), *v.* Anthocyanins.

ŒNOLIN. The name given to the natural red colouring matter of wine precipitable by lime or basic lead acetate. Is brown-red whilst moist, but nearly black when dry, giving a violet-red or brown-red powder, readily soluble in alcohol, and in water acidulated with vegetable acids, *v.* Anthocyanins. For the estimation of œnolin and œnotannin in wines, *v.* F. Jean, Compt. rend. 93, 966.

ŒNOMETER. A hydrometer designed for determining the alcoholic strength of wines.

OIL-GAS *v.* Gas, oil.

OIL, MINERAL, *v.* Petroleum.

OIL OF AMBER *v.* Oils, Essential, and Resins.

OIL OF HARTSHORN *v.* Bone oil.

OIL OF VITRIOL *v.* Sulphuric acid.

OIL OF WINTERGREEN, Methyl salicylate *v.* Oils, Essential.

OILS, ESSENTIAL. The word 'oil' appears to be derived from the Greek *elaion* (oil), *elaia* denoting the olive tree, from the Latin 'oleum,' and the French 'huile.' Three kinds of oil are recognised, fixed or fatty oils, of vegetable or animal origin (*v.* Oils, Fixed, and Fats), which are saponifiable; essential or volatile oils of vegetable origin; and petroleum oils of mineral origin, which are unsaponifiable and consist mainly of hydrocarbons.

Essential or volatile oils are aromatic volatile substances of an oily nature usually obtained by the distillation of vegetable products with steam. They are generally liquid, though sometimes semi-solid at ordinary temperatures, slightly soluble in water, soluble in alcohol, ether, benzene, light petroleum, and most organic solvents. They are found in all parts of the plant or tree, some occurring in the woody stems or roots, others in the bark, leaves, flowers, and fruits. Many essential oils are of complex composition, containing constituents belonging to various classes of organic compounds, terpenes, alcohols, esters, aldehydes, ketones, phenols, &c. In some cases the oil consists almost entirely of one constituent, *e.g.* bitter almond oil (benzaldehyde), black mustard oil (allyl iso-thiocyanate), and wintergreen oil (methyl salicylate). Each of these three oils is formed by the decomposition of a glucoside by a natural ferment or enzyme which exist together in the material, the reaction being induced by maceration in water with the formation of glucose as a by-product.

The general characters of essential oils extend over a wide range, the specific gravity in most cases being less than 1·000, though several oils are known which are heavier than water. The refractive indices vary from 1·432 (rue oil) to 1·605 (cassia oil). Many oils are optically active to polarised light, the optical rotation being a character of importance for judging purity, each individual oil having a comparatively small natural variation.

The functions of the essential oil in the plant economy are not thoroughly understood. In some cases its fragrant odour has an attraction for certain insects which fertilise the flower, in others it acts as a repellant against enemies of the plant.

Some oils apparently result from pathological processes, others appear to be by-products of metabolic processes of an obscure nature. The development of the essential oil in several plants has been investigated by Charabot and his pupils, who have studied the effect of different manures on the yield and character of the oil from peppermint plants, the influence of light, climate and soil, and the best period of collection for distillation.

Essential oils are usually secreted in special glands, cells, or vessels, and are frequently associated with resinous bodies. For example, turpentine oil is obtained by the distillation of the oleo-resin or turpentine which is secreted in the resin-ducts of pine trees. Many oils become resinous on exposure to air, chiefly owing to the oxidation of the terpene constituents.

According to Charabot the odorous compounds first appear in the young green organs of plants, and continue to form and accumulate until the flowering period, when the activity slackens. They migrate by diffusion from the leaf to the stem, and thence into the inflorescence. A portion enters into solution and penetrates into the tissues where it becomes deposited. When fertilisation takes place, a quantity of essential oil is consumed in the inflorescence, or is lost by evaporation. Probably the green organs continue to produce odorous constituents, but experiments show that during fertilisation there is a net loss of these bodies. It is therefore obvious that in most cases the best yield of essential oil is obtained before fertilisation takes place. After fertilisation the oil again increases in the green parts of the plant.

Esters have their origin in the green parts of the plant by the direct combination of acids on the alcohols previously formed. Esterification appears to be assisted by enzymes which act as dehydrating agents. Chlorophyll, however, appears to be the important factor in effecting the condensations which build up complex substances from simpler bodies.

The addition of mineral salts to the soil, such as the chlorides of potassium, sodium and ammonium, sulphates of sodium, potassium, ammonium, iron and manganese, nitrates and phosphates of sodium and potassium, appears to favour the formation of esters in peppermint plants.

In some instances the oils are semi-solid or almost solid in character. Although the words are of little scientific value the solid portion of oils are still described as *stearoptenes*, and the liquid portions as *oleoptenes* or *elæoptenes*.

The methods of production may be divided into three principal classes.

(1) Distillation:

(*a*) From the plant;

(*b*) From oleo-resinous exudations.

(2) Mechanical processes.

(3) Extraction by solvents.

1. The methods of production of volatile oils by distillation from the wood, leaves,

flowers or fruit by means of water, which is the usual method employed, have been greatly modified in recent years, and much attention has been devoted to improvements in modes of distillation and condensation. In some few instances fire heat is still used for distillation, the practice being retained by native distillers of essential oils in tropical countries. The usual method, however, is to pass steam through the material suitably arranged on trays—for example, in the case of the umbelliferous fruits, or to pass live steam through the material.

All the essential oils are readily volatile in the vapour of water. Many oils are distilled from their primary material under reduced pressure, the vapour passing over at a much lower temperature, with the corresponding advantage that the oil is not subjected to temperature likely to lead to decomposition. Modern stills have a capacity of 600–1200 gallons or more, and are usually made of copper with removable domes having water-sealed joints with latch fastenings to keep them in position. They are mounted on brickwork bases with steel framework, and have bottoms raised in the centre to effect absolute drainage. The stills are fitted with discharge pipes and also with steam heating coils constructed of copper with traps for the condensed water, which is led back into a tank for feeding the steam boiler. The still heads taper to a narrow pipe which leads to the condenser. The false bottom and cages in which the material is placed rest upon brackets fitted into the inside of the still. They are usually made of galvanised iron and the false bottom is perforated to enable the water to drain away. Above the stills chain lifting tackle is fitted to steel girders to facilitate emptying and refilling.

The condensers usually consist of coils surrounded by cold water, which is kept continually flowing through them from the bottom upwards. The condensed distillate is collected in separators fitted with strainer plates and a series of draining taps. The condensed water is forced back into the stills by steam ejectors to be used in a subsequent distillation.

Distillation from oleo-resinous exudations. Many of the oleo-resins of different degrees of viscidity are used for the distillation of volatile oils—the most important being the oleo-resin used for the distillation of turpentine, and the essential oil distilled from such bodies as copaiba, &c. In the case of turpentine the oleo-resin is caused to exude from the living tree by making incisions, usually V-shaped, after stripping off the bark. The incisions are first made about 8 inches above the root, and the oleo-resin which exudes is collected in wooden vessels. The exudation commences about March and continues till the end of August or the beginning of September. The crude oleo-resin thus obtained is then distilled with water.

2. *Mechanical production.* Mechanical processes are employed in the case of lemon, orange, bergamot, and lime oils, which are obtained from the peel of the fruit. *The sponge process*, which is usually employed in Sicily, and Calabria, is essentially as follows: The fruit is first soaked in water for a short time and the peel is then removed in three slices, each slice being pressed flat by the fingers against a sponge. The oil glands are burst by the pressure and the oil, together with a considerable quantity of water and some juice, is absorbed by the sponge. The sponge is squeezed from time to time into a bowl and the oil separated from the water and filtered in closed filters.

The Écuelle process is employed in Northern Italy and the South of France. An écuelle is a saucer-shaped vessel, 8–10 inches in diameter, made of tinned copper, the inside of which is covered by short spikes about a quarter of an inch long. The bottom is connected by a hollow tube through which the oil passes to a collecting vessel. The whole fruit is placed on the écuelle and by rapid rotatory motion the oil glands are burst and the oil is ejected. An oil of inferior quality is obtained by subjecting the residual fruits to pressure or by macerating in warm water. A still inferior oil is obtained by distillation.

In the *Scorzetta process* the fruits are cut into halves, the pulp is removed by a spoon and the peel is twisted and pressed against a sponge. The pulp is used for the production of lemon juice and the peel is salted.

Machines are also used for the production of these oils, especially that of bergamot, by means of which the fruits are brought into contact with small knives which puncture or rupture the oil glands. The oil is drawn out of the vessel by means of vacuum pumps and steam is sometimes admitted to facilitate the process. Machine made oils, however, are usually inferior to those produced by hand processes. An illustration of one form of mechanical press is figured in the Perfumery and Essential Oil Record, March, 1910, 61.

3. *Extraction by solvents.* Extraction processes are employed principally for the delicate floral essences which are partially decomposed by distillation, such as jasmine and tuberose. Three kinds of processes are used: (*a*) those in which a volatile solvent is used; (*b*) those in which a non-volatile oil or fat is employed; and (*d*) those in which a current of moist air is used.

The volatile solvents commonly employed are alcohol, benzene, ether, chloroform, light petroleum, dichlor-ethylene, acetone, and tetrachlorethane. The simplest form of extraction is by percolation, either in the cold or at the boiling-point of the solvent on the principle of the Soxhlet apparatus. On the removal of the solvent a mixture of oil, resin, wax and colouring matter results, known as 'concretes,' from which floral essences are prepared by solution in alcohol. In some cases the extracts are purified by distillation under reduced pressure with steam. These are known as 'absolutes.'

The extraction by non-volatile solvents is typified by the *enfleurage process*. A pure neutral fat, such as purified lard, is melted in trays, technically known as 'chassis,' and the fresh flowers are laid on the fat for a short time, then removed and replaced by fresh flowers until the fat has become saturated. The fat is then removed and sold as 'pomades,' which are employed in the manufacture of perfumes, being extracted by means of warm alcohol in closed vessels. Olive oil is also used for jasmine and violet flowers, the fresh flowers being macerated in the oil or placed on trays containing linen cloths soaked in the oil. The oil is then pressed out and may be extracted by means of alcohol or used in brilliantines.

In the *moist air process*, hot air is passed through a series of wet sponges and then over the flowers and into a volatile solvent which retains the perfume, and which can afterwards be removed. The advantage of this process is that only volatile bodies are extracted, colouring matters and resins being left in the raw material.

The main constituents of essential oils may be conveniently divided into the following important classes: terpenes and sesquiterpenes, alcohols, esters, aldehydes, ketones, phenols and allied compounds.

Terpenes. The principal terpenes occurring in essential oils are pinene, camphene, fenchene, limonene, dipentene, terpinene, terpinolene phellandrene, sylvestrene, carvestrene, thujene, sabinene, santene. The first three belong to the bicyclic series, the structure being in the form of a double ring. The other terpenes may be regarded as derivatives of cymene, which they closely resemble in molecular constitution. Limonene, dipentene, carvestrene, sylvestrene, and terpinolene may be regarded as dihydrocymenes, containing two ethylene linkages and have the formula $C_{10}H_{16}$. Menthene and carvo-menthene are tetrahydrocymenes and have the formula $C_{10}H_{18}$. On reduction they yield hexahydrocymenes. The terpenes are characterised by the melting-points of their derivatives.

Sesquiterpenes. These have the general formula $C_{15}H_{24}$ and boil at a temperature above 250°. They have a high refractive index and yield halogen derivatives which are somewhat difficult to purify. The more important ones occurring in essential oils are cadinene, caryophyllene, cedrene, humulene, santalene, and zingiberene. Olefinic sesquiterpenes occur in oils of citronella, lime, and lemon.

For further details as to characters and composition of this class of substances, *see* art. TERPENES.

Alcohols. The alcohols of the paraffin series found in essential oils comprise geraniol, linalool, nerol, and citronellol. These belong to the unsaturated series containing one or more double linkages.

Alcohols of the benzene series are benzyl, cinnamyl, and anisyl alcohols and phenyl-ethyl-alcohol. Terpineol, terpene hydrate, borneol, pulegol, thujyl alcohol, fenchyl alcohol, sabinol, and menthol are derivatives of the terpenes. Among sesquiterpene alcohols, santalol, cedrol, guaiol, patchouli alcohol, and the so-called 'camphors' of cubebs and matico may be mentioned. With the exception of santalol these are solid compounds.

Esters of many of these alcohols also occur in essential oils, notably those of acetic, propionic, butyric, valeric, tiglic, benzoic, salicylic, cinnamic, and anthranilic acids. The percentage of esters is found by saponification with alcoholic potash and many oils are valued according to their ester content. It should be pointed out, however, that probably other constituents absorb potash under the conditions of saponification and the determination of the saponification number is not strictly a measure of the esters present. It is useful, however, for purposes of comparison. Two to five grammes of the oil are heated on a water-bath for an hour with 20 c.c. of normal alcoholic potash and the excess of potash titrated with normal sulphuric acid. The acid value of the oil should be deducted from the saponification value in determining the ester-content.

The alcohols are determined by acetylation and subsequent estimation of the acetic esters formed. The usual method of procedure is to heat 10 c.c. of the oil with 15 c.c. of acetic anhydride and 2 grams of anhydrous sodium acetate for 2 hours to boiling-point under a reflux condenser. The oil is then thoroughly washed by shaking with successive quantities of water and afterwards dried by shaking with anhydrous sodium sulphate. 2–5 grammes of the acetylated oil is then neutralised and saponified with 20 c.c. of normal alcoholic potash for an hour and the excess of potash titrated with normal acid, using phenolphthalein as indicator. The percentage of alcohol in the original oil is calculated from the formula $\frac{M}{1000} \times \frac{X \times 100}{W-(0{\cdot}042X)} =$p.c. alcohol, where M is the molecular weight of the alcohol, W the weight of acetylated oil, and X the number of c.c. of normal alcoholic potash absorbed.

Aldehydes. The aldehydes of the paraffin series found in essential oils are furfural, acetaldehyde, citral, and citronellal. Those belonging to the benzene series are benzaldehyde, salicylic aldehyde, cinnamic aldehyde, anisic aldehyde, and cumic aldehyde.

The usual method employed for the determination of cinnamic aldehyde in cinnamon and cassia oils and for the determination of citral in lemongrass oil is as follows:—

Five c.c. of the oil are shaken with a hot solution of sodium bisulphite (35 p.c.), freshly prepared, and heated in a water-bath for an hour, or until the solid aldehyde bisulphite compound is completely dissolved. A flask with the neck graduated in tenths of a cubic centimetre is employed and the uncombined oil is driven up into the neck of the flask and the volume noted after cooling. The difference between the volume of the original oil and the volume of the residual oil represents the proportion of citral or cinnamic aldehyde, and multiplied by 20 gives the percentage by volume.

For the determination of citral in lemon oil the hydroxylamine process is recommended (*see* Perfumery and Essential Oil Record, November 1910, 263–264).

Ketones. The more important ketones occurring in essential oils are carvone, pulegone, menthone, camphor, fenchone, and thujone. Methyl-heptyl-ketone and methyl-nonyl-ketone occur in the oil of rue and methyl-heptenone in the oils of lemongrass, citronella, and lignaloe.

The best absorption process for the estimation of carvone is as follows:—

Five c.c. of the oil is introduced in a 200 c.c. flask with the neck graduated in tenths of a cubic centimetre. 25 c.c. of a 20 p.c. solution of neutral sodium sulphite is then added and a few drops of phenolphthalein solution. It is then placed in a water-bath and thoroughly shaken, when a red colour is immediately produced due to the liberation of free caustic alkali. A 10 p.c. solution of acetic acid is added from a burette to maintain neutrality, and the mixture heated until no more free alkali is liberated, the time required being usually about 45 minutes. The uncombined oil is then driven into the neck of the flask and the volume read off after cooling. The difference between the volume of the original oil and that of the residual oil multiplied by 20 will give the percentage by volume of carvone. For pulegone in oil of pennyroyal litmus is a better indicator, and four hours are required for complete absorption.

The above process may also be used for the determination of benzaldehyde in almond oil, cinnamic aldehyde in cinnamon and cassia oils, and citral in lemongrass oil.

Phenols (*v. also* art. TERPENES AND TERPENE DERIVATIVES). The chief phenols found in essential oils are thymol, carvacrol, and eugenol (*q.v.*). These bodies are soluble in solutions of alkaline hydroxides, and may be extracted by shaking the oils with a solution of caustic potash or soda. They differ from acids in not being soluble in alkaline carbonates.

The method usually adopted for the estimation of phenols in essential oils is as follows: 5 c.c. of the oil is heated for an hour in a water-bath with a 5 p.c. aqueous solution of potash with frequent agitation. A flask with the neck graduated in tenths of a cubic centimetre is employed for the purpose, and the uncombined oil is driven into the graduated neck by the addition of a further quantity of potash solution. The proportion of phenols absorbed is calculated by deducting the measure of uncombined oil from the volume of the original oil, which gives the proportion of phenols by volume. If the proportion by weight is required the specific gravity of the oil and the uncombined portion must be taken into account.

Phenol derivatives. Anethole is the methyl ether of *p*-propenyl phenol. It is the chief constituent of anise oil and star anise oil and also occurs in oil of fennel. It is a crystalline substance, melting at 21° and boiling at 232°; sp.gr. 0·986 at 25°.

Iso-anethole (*estragole*) is the methyl ether of *p*-allyl-phenol. It occurs in estragon oil, and also in anise and fennel oils. It is a colourless liquid having a density of 0·971 and boiling at 215°–216°.

Safrole is the methylene ether of allyl-pyrocatechol. It is the principal constituent of sassafras oil, and occurs in the high-boiling fractions of camphor oil and in cinnamon leaf oil. It is a colourless liquid, boiling at 233°; sp.gr. 1·108.

Other phenol derivatives are diosphenol, found in oil of buchu, chavicol, a constituent of bay oil and betel leaf oil, and chavibetol, occurring in betel leaf oil.

Unclassified constituents of essential oils. Apiole occurs in oil of parsley and its isomer dill-apiole in East Indian oil of dill.

Cineole or eucalyptol occurs in oils of wormseed, cajeput, and eucalyptus, and in smaller quantities in oils of rosemary, lavender, spike, sage, laurel, cinnamon, and camphor.

Compounds containing nitrogen and sulphur occur in essential oils derived from plants rich in albuminous matter. The more volatile compounds, such as trimethylamine and sulphuretted hydrogen (the latter being formed during the distillation of carraway oil) are usually lost in the distillation process.

Hydrocyanic acid occurs together with benzaldehyde in oil of bitter almonds. Carbon disulphide is found in black mustard oil, dimethyl sulphide in American peppermint oil, and allyl di-sulphide in oil of garlic. Allyl-*iso*thiocyanate is the chief constituent of black mustard oil, resulting from the decomposition of the glucoside potassium myronate in the presence of the ferment myrosin. It is obtained synthetically from allyl iodide and potassium thiocyanate.

EXAMINATION OF ESSENTIAL OILS.

Physical characters. In the analysis of essential oils it is usual to first determine the physical characters, such as the specific gravity, optical rotation, refractive index, boiling range, and solubility.

The *specific gravity* is the density at 15° compared with the weight of an equal volume of water at the same temperature, and is usually taken by means of a specific gravity bottle of 10 c.c. or 25 c.c. capacity. Anise oil and otto of rose are generally taken at 20° and 30° respectively in comparison with water at 15°C. Oils which contain water should be first dried by agitation with anhydrous sodium sulphate.

Optical rotation. The optical rotation of essential oils is usually taken in a 100 mm. tube by means of a polarimeter, using sodium light. The specific rotation applied to pure substances is the optical rotation in a 100 mm. tube divided by the specific gravity. It is expressed by the term $[\alpha]_D$.

The refractive index is the ratio of the sine of the angle of incidence to the sine of the angle of refraction for the D line (sodium light) and is expressed by the term n_D. It is usually given for a temperature of 20° and decreases with rise of temperature to the extent of 0·0004 to 0·0006 for each degree Centigrade. Refractometers are of various types, but the direct reading instrument made by Zeiss is the one most suitable for the examination of essential oils (*v.* REFRACTOMETER). The temperature is kept constant by passing a stream of water through the two prisms between which the oil is placed.

The melting-point of an oil is best determined by placing about 3 c.c. in a test-tube, and congealing it by immersion in a freezing mixture. The tube is then immersed in a beaker of water and the temperature of the water slowly raised until the oil is just completely melted, a thermometer being used to stir the oil continuously. For crystalline solids the capillary tube method should be employed.

The boiling-point of a substance depends on the pressure of the atmosphere, the standard pressure being equal to 760 mm. of mercury. The correction for variation of pressure is made as follows: $T=T_1+0{\cdot}0375\ (760-p)$ where T is the true boiling-point, T_1 the observed boiling-point, and p the observed pressure. For accurate determination a correction may be made for the portion of the stem of the thermometer not surrounded by the vapour of the boiling liquid. This is made as follows:

$T=T_1+0{\cdot}000154\,t.d.$ where T is the true boiling-point, T_1 the observed boiling-point, t the number of degrees exposed to the atmosphere, and d the difference between the temperature of the boiling liquid and that of the surrounding atmosphere.

***Fractional distillation* of essential oils is usually carried out under reduced pressure which should not exceed about 25 mm. A three-bulbed flask or a fractionating column is sometimes used, better separations being thus obtained. The characters of the various fractions are exceedingly useful in detecting adulteration.**

Methods for the determination of alcohols, esters, aldehydes, ketones, and phenols are given under the various constituents.

Solubility.—The solubility of an oil is often a good criterion of purity. It is usually determined by shaking 1 c.c. of the oil with 1, 2, 3, or more c.c. of alcohol of various strengths. The strengths generally employed are 70, 80, 90, and 95 p.c., and these must be carefully adjusted to the correct specific gravity. Each oil has a definite solubility value and the test serves to detect adulteration or the presence of oxidised or resinified products. Petroleum floats in 70 p.c. alcohol, fixed oils sink. A definite standard temperature should be adopted, say 20°C.

DETECTION OF ADULTERANTS.

Turpentine oil may be readily detected in oils which contain no pinene, the latter being the chief constituent of turpentine oil. It is usually found in the first fraction distilled, and generally reduces the specific gravity and affects the solubility. Its presence is proved by the formation of pinene hydrochloride (m.p. 125°) and its nitrosochloride (m.p. 103°).

Cedar wood, *copaiba*, and *gurjun balsam oil.* These are usually found in the last fractions since their chief constituents are sesquiterpenes. They have a high refractive index and high specific gravity, and are only soluble in absolute alcohol. Copaiba oil rotates −5° to −35° (African +20°), cedarwood oil −25° to −45°, and gurjun balsam −35° to −130°.

Alcohol may be detected by its low boiling-point, low specific gravity, low refractive index, and by the iodoform test. Oils containing alcohol form milky mixtures with water. It may be extracted by washing the oil with water.

Acetone may be detected in a similar manner.

Fatty oils leave an oily stain when exposed on blotting paper. With the exception of castor oil they are insoluble in alcohol. They usually increase the ester value of an oil and increase the non-volatile residue. Fatty oils have a very high boiling-point, and are therefore found in the residue left on distillation, where they may be detected by the acrolein test.

***Artificial esters* have usually a high boiling-point and may be detected in the last fractions of an oil by saponifying with aqueous potash and identifying the products of hydrolysis.**

Glyceryl acetate, ethyl citrate, tartrate, oxalate, phthalate, and succinate have been used for adulteration purposes.

Petroleum (**mineral oil, kerosene, &c.) is less soluble in alcohol than most oils. It has a low specific gravity and refractive index, and is not saponified by potash. It is also unaffected by nitric and sulphuric acids.**

PRINCIPAL ESSENTIAL OILS.

Absinthe oil (wormwood oil) is distilled from the leaves and tops of *Artemisia absinthium* (*N.O. Compositæ*), a herbaceous plant growing in Europe, Northern Africa, and Northern Asia, and cultivated in the United States of America. The yield is from 0·5 to 1·0 p.c. It is of a dark green or bluish colour and has a sp.gr. of 0·920–0·955. It contains thujone (tanacetone), thujyl alcohol, acetic and valeric esters, phellandrene, pinene, and cadinene. It is used in the preparation of absinthe, in conjunction with other essential oils (*v.* ABSINTHE).

Ajowan oil is distilled from the fruit of *Carum ajowan* (Bentham and Hooker) or *Ptychotis ajowan* (D.C.) (*N.O. Umbelliferæ*). Cultivated in India, Egypt, Persia, and Afghanistan. The yield is from 3 to 4 p.c.; sp.gr. 0·900–0·930; slightly dextro-rotatory. Contains thymol (40–55 p.c.), cymene, and a terpene hydrocarbon. Ajowan oil is the chief source of thymol (methyl *iso*propyl phenol), which is extracted from the oil by freezing or by means of caustic soda, precipitating with hydrochloric acid and recrystallising from alcohol. Thymol melts at 50°–51°, and boils at 230°.

Bitter almond oil. Obtained by distillation with water from the marc left after expression of the fixed oil from the seeds of bitter almonds *Prunus Amygdalus*, var. *amara* (*N.O. Rosaceæ*). The oil results from the action of a nitrogenous ferment *emulsin*, found in both sweet and bitter almonds, on the glucoside amygdalin which exists only in the bitter almond. The reaction occurs in the presence of moisture as follows:—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}}+2H_2O=\underset{\text{Benzaldehyde.}}{C_7H_6O}+\underset{\text{Hydrocyanic acid.}}{HCN}+\underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Benzylcyanhydrin is formed by the interaction of the benzaldehyde with the hydrocyanic acid. The yield of essential oil varies according to the quality of the almonds, and according to the proportion of sweet almonds mixed with the bitter. The marc yields on an average 1 p.c. of oil corresponding to about 0·5 p.c. from the original almonds; sp.gr. 1·045–1·070; it is optically inactive and consists of benzaldehyde (90–95 p.c.), hydrocyanic acid (4–6 p.c.), and benzylcyanhydrin or mandelonitrile ($C_6H_5{\cdot}CH(OH)CN$).

The hydrocyanic acid may be removed by redistillation with lime and ferrous sulphate or by agitation with sodium acid sulphite, crystallising the double salt and distilling the crystals with caustic soda. Essential oil of almonds is very rapidly oxidised on exposure to moist air forming benzoic acid, but when carefully dried by immersing in it a piece of calcium chloride it is said to keep indefinitely. It may be adulterated with artificial benzaldehyde or with alcohol. The former, if free from chlorine compounds, is impossible to detect; the latter is detected by shaking with water and applying the iodoform test to the washings.

A similar oil almost identical in character with oil of bitter almonds is obtained from peach and apricot kernels.

Amber oil is a mixture of terpenes obtained by the destructive distillation of amber. Mixed with rectified spirit and ammonia it was formerly used in medicine under the name *Eau de Luce*. By the action of nitric acid a mixture of resins is produced, formerly known as 'artificial musk.' Genuine oil of amber is now very rarely found in commerce, much of the oil used medicinally for embrocations being obtained from amber resin (*colophony* (*q.v.*)) by destructive distillation.

Anise oil. Distilled from the fruit of *Pimpinella anisum* (Linn.) (*N.O Umbelliferæ*), grown in Europe, and from the fruit of the star anise, *Illicium verum* (Hook.) (*N.O. Magnoliaceæ*), cultivated in China. The latter is the source of most of the anise oil of commerce. The yield of oil from the star anise fruits is 2–4 p.c., that from the pimpinella anise seldom exceeding 2 p.c. The characters and constituents of the two oils are practically identical; sp.gr. 0·975–0·990 at 20°/15°, rising on keeping; 0°–2° seldom dextrorotatory; μ1·552–1·558; soluble in 3 vols. of 90 p.c. alcohol; it congeals about 15°, remelting at 17°–19°. It contains anethole 80–90 p.c., methyl chavicol, anisic aldehyde, anisic acid, anisic ketone, pinene, phellandrene, limonene, cineole, and safrole. Important changes take place in the oil on keeping, the melting-point being lowered and the density increasing. It is employed medicinally as a carminative and expectorant and as a flavouring agent.

Asafœtida oil. Distilled from the gum resinous exudation from the root of *Ferula Assa-fœtida* (Linn.) (*N.O. Umbelliferæ*), and probably other species growing in Persia and Afghanistan. It yields by distillation 3–7 p.c. of oil; sp.gr. 0·975–0·990; rotation about −10°. It contains organic sulphur compounds having the formulæ $C_7H_{14}S_2$. $C_8H_{16}S_2$, $C_{10}H_{20}S_2$, pinene, and a sesquiterpene. The proportion of sulphur compounds present varies according to the species of *Ferula* from which the gum resinous exudation has been obtained.

Bay oil. Distilled from the leaves of *Pimenta acris* (Kostel) (*Myrcia acris* [DC.]) (*N.O. Myrtaceæ*), largely grown in the West Indies. The yield is from 2 to 3 p.c.; sp.gr. 0·950–0·990; rotation −0° 30′ to −2°. It contains eugenol 45–80 p.c. methyl-eugenol, chavicol, methyl-chavicol, pinene, dipentene, phellandrene, myrcene, and citral. When distilled with water the oil separates into two layers, one lighter, the other heavier, than water. These are mixed to obtain a normal oil. It is sometimes adulterated with other eugenol-containing oils, notably those of clove and pimento.

Bergamot oil. Obtained by expression from the peel of the fresh unripe fruit of *Citrus Bergamia* (Risso) (*N.O. Rutaceæ*), cultivated in Calabria and Sicily. The process used for extraction is similar to that used for lemon oil. One hundred fruits yield 2½–3 ozs. of oil, which is limpid and of yellowish or greenish-yellow colour; sp.gr. 0·881–0·886; rotation +8° to +24°, rarely exceeding +18°; esters calculated as linalyl acetate, 36–42 p.c.; non-volatile matter after heating 2 hours on water-bath, 5–6 p.c. It contains linalool, linalyl acetate, octylene, pinene, camphene, limonene, dipentene limene (sesquiterpene), bergaptene (stearoptene). The oil is subject to considerable adulteration with added esters, including terpineol acetate, ethyl citrate, &c., together with terpenes from allied species of citrus.

Buchu oil. Distilled from the leaves of *Barosma betulina* (Bartl. & Wendl.), and other species (*N.O. Rutaceæ*), a shrub indigenous to Cape Colony. It yields from 1 to 2 p.c. of oil; sp.gr. 0·940–0·960. It contains diosphenol, limonene, dipentene, menthene, the constituents varying according to the species of *Barosma* used for distillation (*see* Pharm. J. 3rd series, 796–797).

Cajuput oil. Distilled from the leaves of *Melaleuca Leucadendron* (Linn.) (*N.O. Myrtaceæ*), and other species of melaleuca indigenous to India, North Australia, the Malay Archipelago, and the Molucca Islands. It is a green or bluish-green limpid oil having an aromatic camphoraceous odour resembling eucalyptus oil; sp.gr. 0·919–0·930; rotation 0°–4°. It contains cineole (45–60 p.c.), terpineol, pinene, butyric, valeric, and benzoic aldehydes. The green colour of the oil is due to contamination with copper, which can be removed by distillation or by shaking the oil with a solution of citric or tartaric acid or potassium ferrocyanide.

Calamus oil. Distilled from the rhizome of the sweet flag, *Acorus Calamus* (Linn.) (*N.O. Aroideæ*), found on the banks of many European rivers and cultivated in India. The yield is from 1·5 to 3·5 p.c.; sp.gr. 0·960–0·970; rotation +10° to +35°. It contains pinene and a sesquiterpene and several oxygenated constituents. The Japanese oil is probably derived from the rhizome of *Acorus gramineus* (Soland). It has a density of 0·990–1·000. It is used in the preparation of cordials and liqueurs and in perfumery.

Camphor oil. A by-product in the manufacture of camphor from the wood of the camphor tree, *Cinnamomum Camphora* (Nees & Eberm.) (*N.O. Lauraceæ*), found in China, Japan, and Formosa. The oil varies considerably in character, but may be divided into two distinct classes, (1) the light fractions consisting principally of terpenes, (2) the heavy fractions containing more or less safrole, which is largely used in the preparation of heliotropin: sp.gr. (1) 0·860–0·950, (2) 0·950–1·100; rotation (1) +12° to +32°, (2) 0° to +12°. Camphor oil contains camphor, terpineol, safrole, eugenol, cineole, pinene, phellandrene, dipentene, and cadinene.

Cananga oil *v. Ylang Ylang.*

Caraway oil. Distilled from the fruit of *Carum Carvi* (Linn.) (*N.O. Umbelliferæ*), which is cultivated in England, Holland, Germany, Russia, and Morocco. The yield is from 4 to 6 p.c.; sp.gr. 0·900–0·920; rotation +70° to +82°; refractive index (25°) 1·485–1·497; at least 50 p.c. should distil above 200°. It contains carvol or carvone (50–60 p.c.), limonene, dihydrocarveol, and dihydrocarvone. Much of the oil is partially decarvonised, the carvone being employed extensively for the production of the liqueur 'Kummel' (*v.* LIQUEURS).

Cardamom oil. Distilled from the seeds of *Elettaria Cardamomum* (Maton), var. β (*N.O. Zingiberaceæ*), growing wild, and cultivated in Ceylon, Malabar, and Mysore. The cultivated Ceylon variety furnishes the greater part of the oil of commerce. The yield is from 3 to 8 p.c.;

sp.gr. 0·922-0·950 at 25°; rotation +22° to +46°. The wild Ceylon oil is inferior in quality, having a density of 0·895–0·910 and a rotation of +12° to +13°. Cardamom oil contains cineol (5–10 p.c.), *d*-terpineol, limonene, and terpinene.

Cascarilla oil. Distilled from the bark of *Croton Eluteria* (Benn.) (*N.O. Euphorbiaceæ*), a native of the Bahama Islands; the yield is from 1·5 to 3 p.c.: sp.gr. 0·890–0·930; rotation +2° to +5°. It contains cymene, limonene, eugenol, cascarillic, stearic, and palmitic acids, and two sesquiterpenes.

Cassia oil. Distilled from the bark, leaves, and twigs of *Cinnamomum Cassia* (Blume.) (*N.O. Lauraceæ*), indigenous to Cochin China and cultivated in China. The yield is from 0·5 to 2 p.c.: sp.gr. 1·050–1·065; rotation +1° to −1°; refractive index 1·585 to 1·605; soluble in 3 vols. 70 p.c alcohol. It contains cinnamic aldehyde (75–95 p.c.), cinnamic esters, benzaldehyde and methyl salicyl-aldehyde, salicylic aldehyde, coumarin, salicylic acid, and terpenes. It may be adulterated with resin, petroleum, and fatty oils. The oil is sold in various grades according to cinnamic aldehyde percentage, the lower grades being usually reduced by the addition of resin.

Cedarwood oil. Distilled from the bark of *Juniperus virginiana* (Linn.), the red cedar (*N.O. Cupressineæ*). Often obtained from the waste shavings from the manufacture of cedar pencils: sp.gr. 0·940–0·960; rotation −25° to −45°; refractive index, 1·50–1·51. The chief constituent is cedrene (sesquiterpene) It contains 8–10 p.c. of cedrol or cedar camphor, which is a crystalline sesquiterpene alcohol melting at 78°–80°. It is largely used in perfumery and soap manufacture as a fixative for perfumes, and for microscopic purposes on account of its high refractive index. Cedar leaf oil, obtained from the leaves of *J. virginiana*, is dextrorotatory *+55° to +65°, and has a sp.gr. of* 0·883–0·888. It contains limonene, cadinene, borneol, and *bornyl* esters.

Commercial cedar leaf oil is probably derived from *Thuya occidentalis* (Linn.), and other allied trees. It has a density of 0·860–0·920 and optical rotation −3° to −24°.

Chenopodium oil *v. Wormseed oil.*

Cherry laurel oil is distilled from the leaves of *Prunus Lauro-cerasus* (Linn.) (*N.O. Rosaceæ*), an evergreen shrub indigenous to south-eastern Europe and Asia Minor. It has a density of 1·050–1·065 and contains benzaldehyde, prussic acid, and traces of benzyl alcohol. It differs very little from oil of bitter almonds. It is obtained as a by-product in the preparation of cherry laurel water (B.P.), which is standardised to contain 0·1 p.c. of prussic acid, and is used for medicinal purposes.

Cinnamon oil. Distilled from the bark of *Cinnamomum zeylanicum* (Nees) (*N.O. Lauraceæ*), a native of Ceylon. The yield is from 0·5 to 1 p.c.: sp.gr. 1·000-1·040; rotation 0° to −1°; refractive index 1·565–1·582; soluble in 3 vols. of 80 p.c. alcohol. It contains cinnamic aldehyde (55–75 p.c.), terpenes (phellandrene) and traces of eugenol. Oils containing a high aldehyde content (over 75 p.c.) may contain cassia oil or artificial cinnamic aldehyde. These oils have a higher refractive index than 1·582. English distilled oils have a low specific gravity, low aldehyde content, and a much finer aroma than heavier oils.

Cinnamon leaf oil, distilled from the leaves and twigs of the same tree, contains 75–90 p.c. of eugenol and safrole, and only traces of cinnamic aldehyde: sp.gr. 1·045–1·065; rotation −1° to +1°; refractive index 1·533–1·536. Cinnamon leaf oil distilled in the Seychelles is clove-like in odour and contains 85–95 p.c. of eugenol. The oil distilled from the root contains eugenol, safrole, camphor, benzoic aldehyde, and benzoic esters.

Citron or **cedrat oil.** Obtained by expression from the rind of the fruit of *Citrus Medica* (Linn.) (*N.O. Rutaceæ*). The citron is very similar to lemon oil but contains a slightly higher percentage of citral. It is not now an article of commerce, but efforts are being made to grow the fruit in Corsica for the production of the oil. Factitious oils are offered under both names composed of the oils of other species of *Citrus*.

Citronella oil is distilled from the fresh grass *Andropogon Nardus* (Linn.), (*Cymbopogon Nardus* [Rendle]) (*N.O. Gramineæ*), which is largely grown in Ceylon and in the Straits Settlements. The yield is from 0·5 to 1·0 p.c.; the Ceylon oil has sp gr. 0·900–0·915; rotation 0° to −21°; refractive index 1·470–1·482: the Java oil has sp.gr. 0·885–0·910; rotation 0° to −10°; refractive index 1·465–1·468. Citronella oil contains geraniol, citronellal, camphene, dipentene, limonene, and traces of linalool, borneol, methyl heptenone, methyl eugenol, and sesquiterpenes. It is largely used in cheap soap perfumery. The Ceylon oil contains a large proportion of geraniol, the total acetylisable constituents amounting to 58–65 p.c. In the Java variety the citronellal predominates and the proportion of acetylisable constituents is higher (75–95 p.c.) since citronellal is converted into *iso*pulegol acetate on acetylation. There are at least two varieties of citronella grass cultivated: (1) the 'Lena batu' type; (2) the 'Mahi Penghiri' type. The Ceylon oil is largely adulterated with Russian petroleum, the proportion of 12½–15 p.c. having passed the solubility test which has been long in vogue. Attempts are being made to establish a standard for the sale of the Ceylon oil on geraniol content in the same way as cassia and other essential oils are sold on their percentage of odorous constituents.

Clove oil is distilled from the flower buds of *Eugenia caryophyllata* (Thunb.) (*N.O. Myrtaceæ*), indigenous to the Molucca Islands and cultivated in Zanzibar and Pemba, Sumatra, Penang, Madagascar, Seychelles, Mauritius, and West Indies. The yield is from 15 to 20 p.c.; the stems yield about 6 p.c. It has sp.gr. 1·047–1·065 (eugenol 1·070; caryophyllene 0·908); rotation 0° to −1·30°; refractive index 1·528–1·540; soluble in 3 vols. of 70 p.c. alcohol. It contains eugenol (85–95 p.c.) and eugenol esters, caryophyllene, methyl alcohol, furfural, traces of amyl methyl ketone and methyl benzoate. The oil is very largely used for the production of vanillin.

Copaiba oil is distilled from the oleo-resin or balsam of copaiba, which is an exudation from the trunk of *Copaifera Lansdorfii* (Desf.) and other species of copaiba (*N.O. Leguminosæ*), indigenous to Brazil and northern S. America. The Para variety gives the highest yield of oil (60–65 p.c.), the Bahia yielding about 50 p.c., the Maranham and Maracaibo about 40 p.c.: sp.gr. 0·895–0·918; rotation −7° to −25° (occasionally higher); refractive index 1·495–1·500. It is chiefly composed of sesquiterpenes (caryophyllene). African copaiba oil is dextro-rotatory about +20°, but lævo-rotatory oils can be obtained from the wood of young branches. Gurjun balsam oil has a lævo-rotation of −35° and upwards. It gives an intense violet colour when dissolved in glacial acetic acid and treated with a few drops of nitric acid.

Coriander oil is distilled from the fruit of *Coriandrum sativum* (Linn.) (*N.O. Umbelliferæ*), cultivated in most European countries. Russian, Moravian, and Thuringian fruits yield 0·8–1·0 p.c.; French, Dutch, and Italian 0·4–0·6 p.c.: sp.gr. 0·870–0·885; rotation +8° to +14°; refractive index 1·463–1·467; soluble in 3 vols. of 70 p.c. alcohol. It contains coriandrol (*d*-linalool) and *d*-pinene. The body which gives the characteristic odour is unknown. It may be adulterated with orange and lemon terpenes or turpentine oil, which affect the solubility and the rotation.

Cubeb oil is distilled from the dried unripe fruit of *Piper Cubeba* (Linn.) (*N.O. Piperaceæ*), chiefly imported from Java. The yield is from 10 to 18 p.c.; sp.gr. 0·910–0·930; rotation −25° to −40°; refractive index 1·485–1·496; soluble in 3–10 vols. of 90 p.c. alcohol. It contains dipentene, *l*-pinene, camphene, cadinene, and cubeb camphor, a crystalline sesquiterpene alcohol (m.p. 69°–70°, b.p. 245°).

Cummin oil is distilled from the fruits of *Cuminum Cyminum* (Linn.) (*N.O. Umbelliferæ*), also known as the Roman caraway. It is cultivated in Syria, Morocco, Malta, and the East Indies. The yield is from 2·5 to 4·0 p.c.; sp.gr. 0·910–0·930 (East Indian 0·893–0·899); rotation +4° to +8°; good oils dissolve in 3 vols., but inferior oil may require 8–10 vols. of 80 p.c. alcohol. It contains cuminic aldehyde (cuminal) 20–30 p.c., cymene, and a dextro-rotatory terpene, b.p. 156°, probably pinene.

Dill oil is distilled from the fruit of *Anethum* (*Peucedanum*) *graveolens* (Benth. & Hook.), *N.O. Umbelliferæ*. Indigenous to the Caucasus and Mediterranean countries, cultivated in Bavaria, Thuringia, and Roumania. The yield is from 3 to 4 p.c.; sp.gr. 0·895–0·915 (usually over 0·900); rotation +70° to +80°; refractive index 1·477–1 488; soluble in 3 vols. of 90 p.c. alcohol, 5–8 vols. of 80 p.c. alcohol. It contains carvone (40–60 p.c.), limonene, and phellandrene, but no dill apiol. East Indian and Japanese dill oils obtained from *Anethum* (*Peucedanum*) *Sowa* (Roxb.) have a sp.gr. 0·948–0·970, and a rotation of +41° to +51°. They contain dill apiol, a body heavier than water, b.p. 285°.

Eucalyptus oil. Distilled from the leaves of many species of *Eucalyptus* (*N.O. Myrtaceæ*), that of *Eucalyptus globulus* (Labill.) being chiefly prized though the oils of other species often contain more eucalyptol. The bulk of the oil of commerce is now derived from *E. dumosa* (A. Cunn.), but several hundred species are known and employed for distillation. *See* Baker and Smith's Researches on the Eucalypts, new ed. 1920. Indigenous to Australia, Tasmania, and New Zealand; cultivated in Spain, Algeria, and California. The yield is from 0·8 to 1·5 p.c. The following are the characters of oils of high eucalyptol content as required by the British Pharmacopœia: sp.gr. 0·910–0·930; rotation +10° to −10°; refractive index 1·469–1·475; cineole (eucalyptol) 55–80 p.c.; most oils are soluble in 3–5 vols. of 70 p.c. alcohol. Oils containing much phellandrene and but little cineole such as that of *E. amygdalina* (Lab.) have a lower density (0·855–0·890) and a higher lævo-rotation (−25° to −80°). Eucalyptus oil contains cineole (eucalyptol), pinene, phellandrene, cymene, piperitone, aromadendrene, aromadendral, esters of eudesmic acid, eudesmol or eucalyptus camphor, and traces of amyl alcohol, valeric, butyric, and caproic aldehydes. The medicinal reputation of eucalyptus oil was largely founded on oils from *E. amygdalina*, which are of low eucalyptol content. It is not by any means proved that the value of the oil is dependent on eucalyptol.

The oils of *Eucalyptus citriodora* (Hook.) and *E. maculata* (Hook.) do not contain cineole, but consist almost entirely of citronellal. They have sp.gr. 0·865–0·905; rotation, 0° to +2°. Oil from *E. macarthuri* contains geranyl acetate.

Fennel oil. Distilled from the fruits of *Fœniculum vulgare* (*F. capillaceum*), *N.O. Umbelliferæ*), cultivated in Germany, France, Italy, Roumania, India, and Japan.

Yield.—4–6 p.c.

Characters.—Sp.gr. 0·960–0·990; optical rotation, +6° to +24°; refractive index, 1·525–1·534; m.p. 3°–6°; solubility 1 in 5 to 8 vols. of 80 p.c alcohol.

Constituents.—Anethol (50–60 p.c.), fenchone, *d*-pinene, and dipentene.

Remarks.—*Oil of Sweet Fennel* (*F. dulce*) has a higher anethol content, but does not contain fenchone. *Oil of Bitter Fennel* is derived from the wild plant growing in France, Spain, and Algeria. It contains much *d*-phellandrene and some fenchone, but no anethol. It has a lower density (0·900–0·925) and a higher optical rotation (41° to 48°) than the true fennel oil. *Oil of Water Fennel*, derived from the fruit of *Phellandrium aquatica*, contains a high proportion of phellandrene. It has a density of 0·850–0·890 and an optical rotation of 12°–16°.

For particulars of fennel fruits and their essential oils, *see* Pharmaceutical Journal, 4th series, vol. iii. p. 91; *also* vol. iv. p. 225.

Geranium oil (*Rose-Geranium oil* or *Pelargonium oil*) is distilled from the leaves of *Pelargonium odoratissimum* (Soland), *P. capitatum* (Soland), and *P. roseum* (R. Br.) (*N.O. Geraniaceæ*). Indigenous to South Africa, but largely cultivated in France, Spain, Algeria, and the island of Reunion. The yield is 0·15–0·35 p.c.; soluble in 3 vols. of 70 p.c. alcohol.

Geranium oil contains geraniol, citronellol, and probably linalool, acetic, butyric, tiglic, and valerianic esters. The Spanish oil commands the highest price. The French and Algerian oils come next, and the Bourbon, which is usually darker in colour and has a characteristic odour, is generally of lowest value (*v.* table on p. 640).

—	French	Algerian	Reunion (Bourbon)	Spanish
Sp.gr.	0·895–0·905	0·890–0·900	0·890–0·895	0·889–0·898
Rotation	−7° to −15°	−6° to −12°	−8° to −11°	−10° to −15°
Refractive index	1·465–1·468	1·465–·1470	1·461–1·466	1·465–1·470
Esters calculated as geranyl tiglate	22–28 p.c.	20–29 p.c.	27–34 p.c.	35–42 p.c.
Total alcohols as geraniol	about 75 p.c.	about 75 p.c.	about 80 p.c.	about 70 p.c.

Indian geranium oil (*Turkish Geranium oil*) *v. Palmarosa oil*

Ginger oil is distilled from the rhizome of *Zingiber officinale* (Rosc.) (*N.O. Zingiberaceæ*): indigenous to tropical Asia, and cultivated in the East and West Indies and in Africa. The yield is from 1 to 3 p.c.; sp.gr. 0·872–0·885; rotation −25° to −45°; refractive index 1·4885–1·4950. It contains phellandrene, camphene, and a sesquiterpene zingiberene, also traces of cineole, borneol, and citral.

Ginger grass oil is allied to palmarosa oil. Its botanical source has been traced to *Cymbopogon Martini* (Stapf), var. *motia* (*N.O. Gramineæ*). It has sp.gr. 0·930–0·945; rotation + 29° to +54°; esters 10–25 p.c.; total alcohols calculated as geraniol 35–70 p.c. It contains geraniol, geranyl acetate, dihydrocuminol, and traces of limonene, dipentene, phellandrene, carvone, and an aldehyde not identified.

Juniper oil is distilled from the berries of *Juniperus communis* (Linn.) (*N.O. Coniferæ*) and is produced chiefly in Hungary, where it is obtained as a by-product in the manufacture of gin. The Italian berries produce the best yield of oil, viz. 1–1·5 p.c. The oil has sp.gr. 0·860–0·890, increasing with age; rotation - 3° to −15°, occasionally slightly higher; refractive index 1·472–1·488; soluble when freshly distilled in 4 vols. of 95 p.c. alcohol. It contains pinene, cadinene, juniper-camphor, and a small proportion of esters. Pinene occurs to the extent of 25–60 p.c., and cadinene to the extent of 15–25 p.c. Juniper-camphor consists of a sesquiterpene alcohol (m.p. 165°–166°).

Lavender oil. The variety principally used in commerce is distilled from the fresh flowering herb *Lavandula vera* (DC.) [*L. officinalis* (Chaix.)] (*N.O. Labiatæ*), and other species growing on the higher slopes of the Alps. The distillation is carried out on the spot by means of portable stills, to save cartage of the fresh herb. The oil distilled in the lower districts is inferior to that of the higher. It has sp.gr. 0·883–0·895 (occasionally higher); rotation −3° to −9°; esters calculated as linalyl acetate 25–45 p.c.; total alcohols as linalool 60–70 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, geraniol, nerol, linalyl acetate, pinene, limonene, traces of cineole and thymol and a small quantity of sesquiterpene.

English lavender oil, distilled in Surrey, Suffolk, and Hertfordshire, has similar characters, but contains only 6–10 p.c. of esters calculated as linalyl acetate. Very little English oil is now distilled and its price is very high. It contains more cineole than the French oil, which may be adulterated with artificial esters, ethyl oxalate, citrate, tartrate, benzoate, succinate, benzyl benzoate, &c. Admixture with spike oil is detected by the odour, and by the reduction of ester percentage.

Spike lavender oil or *spike oil* is distilled from the flowering herb *Lavandula Spica* (Cav. Desc.), which grows in the lower mountainous regions of France, Spain, and Italy. Sp.gr. 0·905–0·915; rotation −1° to +4°; total alcohols calculated as borneol 25–45 p.c.; esters as linalyl acetate 4–6 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, borneol, camphor, cineole, terpineol, *d*-camphene, and a sesquiterpene.

Lemon oil is obtained by mechanical means from the fresh peel of *Citrus Limonum* (Risso) (*N.O. Rutaceæ*), which is largely cultivated in Southern Italy and Sicily. It is also grown in Spain, Portugal, Southern France, and in the West Indies, California, and Australia. It is produced in Sicily between November and March. Sp.gr. 0·857–0·862; rotation +57° to +65°; refractive index (25°) 1·473–1·476. Contains limonene (about 90 p.c.), pinene (traces), citral (4–5 p.c.), octyl, nonyl, and decyl aldehyde, geraniol and linalool, and their acetic esters, camphene, phellandrene and a sesquiterpene, limene, identical with bisabolene.

Lemongrass oil *v. Verbena oil.*

Lime oil is obtained by mechanical means from the peel of the fresh fruit of *Citrus Limetta* (Risso) (*C. Medica*) (*N.O. Rutaceæ*), and is produced in Italy in December and January. It resembles oil of lemon in odour, but the citral odour is more pronounced: sp.gr. 0·872–0·885; rotation +35° to +40°; refractive index 1·476–1·485. Contains pinene, limonene, dipentene, citral (6–10 p.c.), linalool and its acetic ester, and limettin (m.p. 147°).

Distilled lime oil is an oil of inferior quality obtained by distillation from the peel of the fruits of *Citrus Medica*, var. *acida*, grown in the West Indies, chiefly Montserrat: sp.gr. 0·856–0·868; rotation +34° to +54°; refractive index 1·470–1·473. Contains pinene, limonene, dipentene, cymene, terpineol, and a sesquiterpene, limene (bisabolene).

Myrtle oil is distilled from the leaves of *Myrtus communis* (Linn.) (*N.O. Myrtaceæ*), grown in Spain, Italy, the South of France, and Cyprus. It is a yellowish or greenish oil with a pleasant odour: sp.gr. 0·890–0·915; rotation +10° to +30°. Contains pinene, dipentene, cineole, and a camphor $C_{10}H_{16}O$, b.p. 195°–200°. The fraction, b.p. 160°–180°, is sold as *myrtol*, and contains cineole.

Mustard oil is obtained from the seeds of the black mustard, *Brassica nigra* (Koch) (*N.O. Cruciferæ*) after expressing the fixed oil. The pressed cake is macerated in water at 60°–70° for several hours, when a reaction takes place between the glucoside *sinigrin* (potassium myronate) and the ferment *myrosin* with the production of essential oil of mustard. It is a colourless or pale yellow mobile liquid, with an intensely pungent odour and blistering properties: sp.gr. 1·014–1·032; refractive index 1·525–1·535; optically inactive; distils between 148° and 156°. It consists almost entirely of allyl *iso*thiocyanate $C_3H_5N:C:S$ (95–99 p.c.), with traces of allyl cyanide. Artificial mustard oil is prepared by distilling allyl iodide with an alcoholic solution of potassium thiocyanate.

Nutmeg oil is distilled from the seed of *Myristica fragrans* (Houtt.) (*N.O. Myristicaceæ*). Indigenous to the Molucca, Banda, and Sunda Islands. The yield is from 8 to 15 p.c. Sp.gr. 0·865–0·930; rotation +10° to +28°. Contains pinene, camphene, dipentene, terpineol, myristicol (a mixture of alcohols, terpineol, linalool, borneol, and geraniol), myristicin, and *iso*myristicin, myristic acid, safrol, eugenol, *iso*eugenol, esters of formic, acetic, butyric, and octoic acids.

Oil of mace is practically indistinguishable from it, the oil being almost identical in character and composition. It is derived from the *arillus* of the nutmeg fruit.

Orange oil is obtained by expression from the peel of the fresh fruit. It consists principally of two kinds, the sweet oil from *Citrus Aurantium* (Linn.), and the bitter oil from *C. Bigaradia* (Loisel.) (*N.O. Rutaceæ*), the latter being usually of somewhat higher value. The tree is indigenous to Southern Asia, but largely cultivated in Southern Europe, Northern Africa, and the West Indies. The two oils are only distinguishable by odour. The bitter oil has sp.gr. 0·848–0·853, and rotation +91° to +98°. The sweet oil has sp.gr. 0·846–0·852, and rotation +96° to +99°. *Oil of Mandarin orange* derived from *Citrus Bigaradia*, var. *sinensis*, which is cultivated in China, has a density of 0·852–0·859, and an optical rotation of +65° to +75°. *Oil of Tangerine orange* has characters almost identical. Orange oil consists principally of limonene (over 90 p.c.), with small quantities of citral, citronellol, decyl, aldehyde α-terpineol, linalool, methyl anthranilate, and citraptene.

Orange flower oil (*Neroli oil*) is distilled from the fresh flowers of the bitter and sweet orange, the former being known as '*Bigarade*,' the latter as '*Portugal*.' It is principally distilled in the South of France. The petals are separated from the sepals, covered with water and heated by a coil of steam pipes. The aqueous distillate separated from the oil is sold as orange flower water. The oil has sp.gr. 0·870–0·885; rotation +0° to +5°; ester content 7–12 p.c. Contains limonene, pinene, dipentene, terpineol, linalool, geraniol, and nerol and their acetic esters, methyl anthranilate and paraffin hydrocarbons.

Orange leaf oil, generally known as *Petitgrain oil*, since it was originally obtained from the small immature fruits, is now distilled from the leaves and young shoots of the bitter and sweet orange, the former commanding the higher price. The best oil comes from the South of France, Spain, and Algeria; a slightly inferior quality is exported from Paraguay. The French oil has sp.gr. 0·885–0·900; rotation −5° to +3°; esters calculated as linalyl acetate 50–85 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains limonene, linalool, geraniol, nerol, and their acetic esters, a sesquiterpene and stearoptene. The Paraguay oil has sp.gr. 0·884–0·895; rotation −2° to +8°; esters calculated as linalyl acetate, 35–65 p.c.; soluble in 1 in 3 vols. 80 p.c. alcohol. Contains pinene, dipentene, camphene, and esters of terpineol and geraniol.

Origanum oil *v. Thyme oil.*

Peach kernel oil *v. Bitter almond oil.*

Palmarosa oil or **Indian geranium oil,** sometimes incorrectly termed *Turkish geranium oil*, is distilled from the grass *Andropogon Schœnanthus* (Benth.) (*Cymbopogon martini*, var. *Sofia*) (*N.O. Gramineæ*), a plant widely distributed in India and found also in tropical Western Africa. It has sp.gr. 0·885–0·895; rotation −2° to +2°; esters 5–11 p.c.; total alcohols calculated as geraniol 75–95 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains geraniol, acetic and caproic esters, and traces of citronellol, methyl heptenone, and dipentene. The oil is now sometimes mixed with certain oils rich in geraniol produced from other grasses.

Parsley oil is distilled from the fruit of *Carum Petroselinum* (Benth. and Hook.) (*Petroselinum sativum*) (*N.O. Umbelliferæ*), indigenous to Asia Minor and the Mediterranean countries, cultivated in all moderate climates. It is colourless, yellowish or yellowish-green, partially solid at ordinary temperatures: sp.gr. 1·050–1·100; rotation −5° to −10°. Contains apiol (m.p. 30°, b.p. 294°) and terpenes, probably *l*-pinene. The oil from the root is similar in character, whilst that from the fresh herb has a lighter specific gravity.

Patchouli oil is distilled from the fresh and dried leaves of *Pogostemon Heyneanus* (Benth.) (*P. Patchouly*, Benth.) (*N.O. Labiatæ*), which is cultivated in the Straits Settlements and in the West Indies. The Java oil is probably derived from a different species. It has sp.gr. 0·950–0·995; rotation −40° to −68°; patchouli alcohol, $C_{15}H_{26}O_2$, soluble in 10 vols. of 90 p.c. alcohol. Contains patchouli alcohol (m.p. 56°), also termed patchouli camphor, cadinene, benzaldehyde, and cinnamic aldehyde.

Pennyroyal oil is obtained from the fresh herb, *Mentha Pulegium* (Linn.) (*N.O. Labiatæ*), and is principally distilled in Spain, Southern France, and Algeria. The oil of American pennyroyal or hedeoma oil is obtained from *Hedeoma pulegioides* (Pers.), which is widely distributed in North America. The two oils are very similar in character; the European oil has sp.gr. 0·930–0·960; rotation +13° to +35°; the American oil has sp.gr. 0·925–0·960; rotation +18° to +22°. Both oils are soluble in 3 vols. of 70 p.c. alcohol and contain pulegone (b.p. 221°–222°) as the chief constituent.

Pepper oil is distilled from the unripe berries of *Piper nigrum* (Linn.) (*N.O. Piperaceæ*), cultivated in Southern India, the Philippines, and the West Indies. It is colourless or yellowish-green, and has sp.gr. 0·870–0·900; rotation −5° to +2°. Consists almost entirely of terpenes and sesquiterpenes, phellandrene being the only constituent actually identified. This oil is rarely met with in commerce.

Peppermint oil is distilled from the fresh and dried flowering herb *Mentha piperita* (Linn.) (*N.O. Labiatæ*), of which several varieties have been obtained by cultivation. The commercial oil can be classified into three distinct varieties, English, American, and Japanese. The English is of two kinds, 'black' and 'white.' The 'white mint' oil is considered superior in quality. The greater bulk of commercial oil is American, but this is inferior to the English oil. Japanese and Chinese peppermint oil is the chief source of menthol, of which it contains from 70 to 90 p.c. Much of the Japanese oil imported has been partially dementholised and contains only about 40 p.c. of total menthol.

Most oils dissolve in 3-4 vols. of 70 p.c. alcohol, but become turbid with more alcohol unless rectified by redistillation. They contain menthol, and menthyl esters, menthone, pinene, phellandrene, cineole, acetaldehyde, dimethyl sulphide, and a sesquiterpene. This oil is now largely distilled in the South of France and Italy from plants originally imported from Mitcham (England). For the characters of the oils and other particulars, *see* Perfumery and Essential Oil Record, 1910, 292-300.

—	English	American	Japanese
Specific gravity	0·900–0·910	0·900–0·920	0·900–0·910
Rotation	– 22° to –33°	–18° to –33°	–30° to –42°
Total menthol	55–66 p.c	50–65 p.c.	70–90 p.c.
Esters calculated as menthyl acetate	Black, 5–7 p.c. White, 8-15 p.c.	— 5–14 p.c.	— 3–6 p.c.

Pimento oil (*oil of allspice* or *Jamaica pepper*) is distilled from the unripe fruit of *Pimenta officinalis* (Lindl.) (*N.O. Myrtaceæ*), indigenous to the West Indies; sp gr. 1·040-1·055; rotation 0° to –4°; phenols 55-75 p.c.; soluble in 3 vols. of 70 p.c. alcohol. Contains eugenol and eugenol methyl ether, cineole, phellandrene, caryophyllene, and palmitic acid.

Pine oils (*Turpentine oil*) (sometimes called spirits of turpentine) are derived from various species of *Pinus* (*N.O. Coniferæ*). The oleo-resin occurs in special resin ducts in the woody portion of the trees. The living tree is 'tapped,' and the oleo-resin or turpentine which exudes is collected. The oleo-resin on distillation with water yields oil of turpentine and the residue is known as *colophony resin*. It is obtained principally in North America, but is also produced largely in Northern Europe and the mountainous districts of Central Europe. American turpentine oil is derived principally from *Pinus palustris* (Mill.) (*P. australis*) and *P. Tæda* (Linn.); the French from *Pinus Pinaster* (Soland); the Russian from *Pinus sylvestris* (Linn.); and the Indian from *Pinus longifolia* (Roxb.). The American is chiefly met with in English commerce; the French variety more commonly on the Continent. Russian turpentine is inferior in quality, as it has a strong characteristic odour and is not easily deodorised. Swedish turpentine is principally derived from *P. sylvestris*, and closely resembles the Russian product.

—	American	French	Russian
Sp.gr.	0·855–0·877	0·855-0·874	0·855-0·874
Rotation	+1° to +6°	–18° to –40°	+5 to +16°

Most turpentine oils dissolve in 5–8 vols. of 90 p.c. alcohol, but the solubility increases with age owing to the formation of soluble oxidation products. They are soluble in an equal volume of glacial acetic acid. Oil of turpentine is composed almost entirely of hydrocarbons, chiefly pinene, with traces of oxidation products such as formic and acetic acids and resin. Camphene and dipentene are usually present and traces of aldehyde. Turpentine oil readily oxidises to resinous substances on exposure to air and light, and on this property depends its use in paints and varnishes.

Pine needle oils or **Pine leaf oils** are obtained from the fresh leaves of various species of *Pinus*. The chief varieties found in English commerce are those of *Pinus Pumilio* (Haenke) and *Abies sibirica*. The oil from *Pinus Pumilio*, official in the British Pharmacopœia of 1898, is distilled in Hungary and the Austrian Tyrol from the leaves and twigs. It contains little pinene, consisting principally of phellandrene and sylvestrene, whilst cadinene has been found in the higher boiling fractions. Only a small proportion of esters is present.

Oil of Abies sibirica is distilled from the fresh leaves and twigs in Northern Russia and the slopes of the Ural mountains. It has a strong characteristic odour and contains 30–40 p.c. of esters chiefly bornyl acetate. It is more soluble than other pine oils, forming a clear solution in an equal volume of 90 p.c. alcohol.

Oil of Pinus sylvestris (*Fir wood oil*) was official in the 1885 edition of the British Pharmacopœia, but the genuine oil is now practically unobtainable. It consists chiefly of *d*-pinene and contains only a small proportion of esters. *Oil of Abies pectinata* (D.C.) [*A. Alba* (Mill.)], is a fragrant oil distilled principally in Switzerland. It contains limonene as well as pinene and a sesquiterpene. The oil from the cones of the same species, known as *templin oil*, is much lighter in density and has a higher optical rotation. It consists principally of limonene.

CHARACTERS OF PINE-NEEDLE OILS.

—	Specific gravity	Rotation	Esters	Distilling between 155°/165°
P. Pumilio . . .	0·863–0·875	–6° to –14°	5–7 p.c.	0–12 p.c.
A. sibirica . . .	0·900–0·930	–32° to – 45°	30–45 p.c.	5- 10 p.c.
P. sylvestris . . .	0·868–0·925	+5° to + 7°	3–11 p.c.	40–65 p.c.
A. pectinata . . .	0·870–0·875	–20° to –60°	5–12 p.c.	0–10 p.c.
A. pectinata (cones) . .	0·853-0·870	–60° to –75°	0–5 p.c.	5–10 p.c.

Pine tar oils are by-products in the manufacture of charcoal and wood tar by the dry distillation of resinous wood. They have an empyreumatic odour and are usually yellow or light brown in colour. They contain pinene, sylvestrene, and dipentene, together with decomposition products. The crude oil is purified by distillation with milk of lime. Pine-tar oil has a sp.gr. of 0·865–0·890, and an optical rotation of +18° to +22°. About 25 p.c. distils below 165°.

Rose oil (*Otto of roses, Attar of roses*) is obtained by distilling the fresh flowers of *Rosa damascena* (Mill.) (*N.O. Rosaceæ*), which is cultivated principally in Bulgaria and on the slopes of the Balkans, and also in France and Germany. It is largely produced by the Bulgarian peasants in primitive stills. It is a light yellow or slightly greenish oil forming a crystalline mass below 18°; sp.gr. 0·851–0·862 at 30°/15°; rotation −2° to −4°; refractive index at 25°, 1·458–1·465; total alcohols calculated as geraniol 65–75 p.c.; m.p. after solidification 18°–22°. The odorous portion is soluble in 70 p.c. alcohol, but the stearoptene is practically insoluble and can be separated by filtration from the alcoholic solution. The odorous portion consists chiefly of geraniol and citronellol (30 to 40 p.c.). Traces of phenyl ethyl alcohol, nerol and farnesol are also present. The odourless stearoptene exists to the extent of 10–16 p.c., and consists of two hydrocarbons melting at 22° and 40° respectively, the mixture melting at about 34°. Otto of roses was formerly much adulterated, and is even now to some extent with geraniol and citronellol and oils containing these bodies (Perfumery and Essential Oil Record, 1910, 188 and 217).

Rosemary oil is distilled from the leaves of *Rosmarinus officinalis* (Linn.) (*N.O. Labiatæ*). Indigenous to the Mediterranean countries, principally France, Spain, and Italy. The leaves are collected after the flowering period and are dried for a few days in the sun before distilling. The oil is produced in limited quantity in Great Britain, this variety commanding a very high price. It has sp.gr. 0·895–0·920; rotation +0° to +15° (sometimes lævo-rotatory); total alcohols calculated as borneol 10–18 p.c.; esters calculated as bornyl acetate 2–6 p.c.; soluble in 10 vols. of 80 p.c. alcohol. Contains pinene, camphene, cineol, camphor, borneol, and bornyl acetate.

Rosewood oil (oil of *Bois de Rose, male*) is obtained by the distillation from the wood of *Licaria guianensis* (Aublet) [? *Ocotea caudata* (Mez.)] (*N.O. Lauraceæ*), collected in French Guiana. A similar oil is obtained from the wood of *Protium altissimum* (March.), known as *Bois de Rose femelle* (*see* Perfumery and Essential Oil Record, 1910, 32). Rosewood oil has sp.gr. 0·870–0·880; rotation −15° to −17°; soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, geraniol, terpineol, nerol, and traces of methyl heptenone.

Linaloe oil (*Lignaloe oil*) is an oil of similar composition obtained from the wood of *Bursera Delpechiana* (Poiss.), *B. Aloëxylon* (Engl.), and other species. It is principally distilled in Mexico: sp.gr. 0·875–0·895; rotation −5° to −12° (sometimes dextro-rotatory); soluble in 3 vols. of 70 p.c. alcohol. Contains linalool, with geraniol, *d*-terpineol, and methyl heptenone.

Rue oil is distilled from the herb *Ruta graveolens* (Linn.) (*N.O. Rutaceæ*), which is indigenous to Europe. Other species are also cultivated in Algeria, *Ruta* (*bracteosa*) *chalepensis* (Linn.) and *R. montana* (Mill.). It has sp.gr. 0·830–0·845; rotation +0° to +2·30°; m.p. +9° to +10°; soluble in 3 vols. of 70 p.c. alcohol. Consists principally of methylnonyl ketone, with some methylheptylketone. Traces of methyl anthranilate give the fluorescent appearance to the oil. Algerian oil from *R. bracteosa* consists principally of methylheptylketone and does not solidify.

Sage oil is distilled from the fresh leaves of *Salvia officinalis* (Linn.) (*N.O. Labiatæ*). Indigenous to the Northern Mediterranean countries: sp.gr. 0·910–0·930; rotation +10° to +25°; soluble in 3 vols. of 80 p.c. alcohol. The Spanish oil has a lavender-like odour and contains linalool probably derived from admixture with lavender plants. Oil of 'clary sage,' *Salvia sclarea*, is employed in perfumery, but the supply is limited.

Sandal-wood oil is distilled from the wood of *Santalum album* (Linn.) (*N.O. Santalaceæ*). Indigenous to the mountains of India and cultivated under Government control: sp.gr. 0·973–0·985; rotation −13° to −21°; total santalol 90–96 p.c.; soluble in 6 vols. of 70 p.c. alcohol at 20°. Contains santalol, a mixture of two sesquiterpene alcohols $C_{15}H_{24}O$, santalal (an aldehyde), santalene, and santene.

West Indian sandal-wood oil, derived from *Amyris balsamifera* (Linn.), is lighter in density (0·960–0·967), and has a rotation of +24° to +29°. It differs in composition from the East Indian oil.

West Australian Sandal-wood oil, derived from *Fusanus spicatus*, R. Br. has a density of 0·955–0·965, rotation −5° to +5°, and contains 65–75 p.c. of total alcohols calculated as santalol. By fractionation, an oil approaching the British Pharmacopœia characters for sandal-wood oil has been produced, but its composition is not identical with that of the East Indian oil, and its medicinal properties have not been satisfactorily established.

Sassafras oil is distilled from the root of *Sassafras officinale* (Nees.) (*Laurus Sassafras* (Nees.)) (*N.O. Lauraceæ*), a native of North America, Canada, the United States, and Mexico. The best yield of oil is obtained from the root bark: sp.gr. 1·065–1·095; rotation +1° to +4°; soluble in 3 vols. of 90 p.c. alcohol. Contains safrol (80–90 p.c.), pinene, phellandrene, camphor, eugenol, and cadinene. Safrole can be separated by fractional distillation and cooling, but commercial safrole is usually obtained from camphor oil.

Savin oil is distilled from the fresh leaves and twigs of *Juniperus Sabina* (Linn.) (*N.O. Coniferæ*). Distilled in Great Britain and Germany: sp.gr. 0·910–0·930; rotation +40° to +68°; esters calculated as sabinyl acetate 36–47 p.c.; total sabinol 45–55 p.c. Contains sabinol, and sabinyl acetate, pinene, sabinene, furfural, decyl aldehyde, dihydro-cuminol, cadinene. French savin oil is derived from *J. phœnicea* (Linn.) and contains a large percentage of pinene. It is lighter in density (about 0·890), has a much lower rotation (+4° to +5°) and contains only about 10 p.c. of esters and 17 p.c. of total sabinol.

Spearmint oil is distilled from the fresh herb *Mentha viridis* (Linn.) (American) and *Mentha crispa* (Linn.) (German), and probably other species of *Mentha* (*N.O. Labiatæ*): sp.gr. 0·920–0·960; rotation −36° to −48°; soluble in an equal volume of 90 p.c. alcohol, but becoming opalescent on dilution. Contains carvone, phellandrene, limonene, pinene, and traces of valerianic esters. The body having the characteristic odour, according to Elze, is the acetic ester of dihydrocuminol.

Star anise oil *v. Anise oil.*

Tarragon oil or **Estragon oil** is distilled from the flowering herb *Artemisia Dracunculus* (Linn.) (*N.O. Compositæ*). Indigenous to Siberia and cultivated in Europe, used in the manufacture of sauces: sp.gr. 0·890–0·960; rotation +2° to +9°; soluble in 10 vols. of 80 p.c. alcohol. Contains estragol (methyl chavicol), phellandrene, *p*-methoxycinnamic aldehyde, and an olefinic terpene.

Terebene *v. Terpenes.*

Thyme oil. Red Thyme oil is distilled from the fresh flowering herb *Thymus vulgaris* (Linn.) (*N.O. Labiatæ*). It is principally grown in the mountainous parts of Southern France. Spanish thyme oil is probably derived from a species of *Origanum*, as it contains carvacrol but little thymol. Oil of wild thyme from *Thymus serpyllum* contains but a small proportion of phenols. French oil has sp.gr. 0·905–0·950; rotation (after redistillation) 0° to −2°; phenols absorbed by 5 p.c. solution of potash 20–45 p.c.; Spanish oil has sp.gr. 0·930–0·950; phenols absorbed by 5 p.c. solution of potash 40–70 p.c. Thyme oil is soluble in 2 vols. of 80 p.c. alcohol, and contains thymol and carvacrol, cymene, pinene, borneol, and linalool.

Origanum oil is distilled from various species of origanum, the oil imported from Trieste being chiefly derived from *Origanum hirtum* (Link.), that from Asia Minor from *O.* (*smyrnæum*) *Onites* (Linn.), and Cyprus oil from *Origanum Majoranoides* (Linn.) (*N.O. Labiatæ*).

—	Trieste	Smyrna	Cyprus
Sp gr. . .	0·940–0 980	0 915 -0 945	0 960 -0 970
Rotation .	0° to −1°	-3° to -13°	—
Phenols (absorbed by 5 p.c. solution of potash) .	60–85 p.c.	25 -60 p.c	78 -84 p.c.

All are soluble in 3 vols. 70 p.c. alcohol and contain carvacrol and cymene; Smyrna oil contains linalool; Cyprus oil contains origanene and traces of hydroxymethoxycymene. Oils of good quality contain over 65 p.c. of phenols.

Verbena oil. True vervain oil is distilled from the leaves of *Verbena triphylla* (L'Hérit.) (*Lippia Citriodora* (H. B. & K.)), which is cultivated for decoration purposes in Spain and the South of France, the oil being distilled only in small quantities: sp.gr. 0·894–0·918; rotation −12° to −16°; contains 21–28 p.c. of citral.

Indian verbena oil or **lemongrass oil** has largely replaced the true verbena oil, as it contains a higher percentage of citral. It is distilled from the grasses *Cymbopogon citratus* (Stapf) and *C. flexuosus* (Stapf). The former is the source of the Ceylon and Straits Settlements oil, the latter of the Malabar and Cochin. *C. citratus* is also cultivated in the West Indies, but the West Indian oil is lighter in density and less soluble than the East Indian variety.

——	East Indian	West Indian
Sp.gr. .	0·895–0·905	0·877–0 887
Rotation .	+3° to −3°	+2° to −2°
Solubility .	1 in 3 volumes of 70 p.c. alcohol	Not soluble in 90 p.c. alcohol

The chief constituent is citral, of which good oils contain 75–85 p.c. Other constituents are methyl heptenone, limonene, and dipentene. An oil of similar constitution, and containing a still higher percentage of citral, is derived from the leaves of *Backhousia citriodora* (F. Muell.) (*N.O. Myrtaceæ*), a small tree indigenous to Queensland. It has a sp.gr. of 0·895–0·900, is optically inactive, and contains about 95 p.c. of citral.

Wintergreen oil is distilled from the leaves of *Gaultheria procumbens* (Linn.) (*N.O. Ericaceæ*). Indigenous to the United States. The oil is produced by a kind of fermentation from a glucoside *gaultherin* by the action of an enzyme. It has sp.gr. 1·180–1·187; rotation −0°25′ to −1°. Consists almost entirely of methyl salicylate (over 99 p.c.) with traces of an alcohol, ester, ketone, or aldehyde, and a paraffin hydrocarbon melting at 65°. An oil almost identical with the foregoing is obtained from the bark of *Betula lenta* (Linn.), the sweet birch (*N.O. Betulaceæ*). This is now mainly sold as wintergreen oil. It differs from true wintergreen oil in being optically inactive. Methyl salicylate is produced synthetically on a large scale, and its detection in oil of wintergreen is very difficult (*see* Perfumery and Essential Oil Record, 1915, pp. 105, 125).

Wormseed oil. The European oil is distilled from the expanded flower buds of *Artemisia maritima* (Linn.) (*N.O. Compositæ*) and other species. Indigenous to Southern Russia and the Levant. Owing to the high price of raw material it is very scarce and has been almost entirely superseded by the American oil. Levant wormseed oil has a sp.gr. of 0·915–0·940, and is lævo-rotatory from −1° to −5°. Contains cineole, dipentene, terpinene, terpineol, and a sesquiterpene.

American wormseed oil is derived from the seeds of *Chenopodium ambrosioides*, var. ***anthelminticum.*** It has sp.gr. 0·950–0·990; rotation −3° to −10°; saponification about 8·5 (after acetylation about 280). Contains cymene, terpinene, and ascaridole (60–65 p.c.), a body closely allied to cineole, decomposing violently on heating to about 150°. Ascaridole has a density of 1·008.

Ylang Ylang oil is distilled from the flowers of *Cananga odorata* (Hook.) (*N.O. Anonaceæ*). Indigenous to the Malay Archipelago and cultivated in the Philippine Islands.

Cananga oil consists usually of the higher fractions and contains a greater proportion of sesquiterpenes, but in some districts the entire oil is sold as cananga oil. The majority of samples fall within the following limits—

—	Ylang Ylang	Cananga	Manila oil
Sp.gr. . .	0 930–0·960	0 910 -0·940	0 900–0 945
Rotation .	–38° to –45°	–17° to –55°	–22° to –50°
Sapon. No. .	95–130	45-100	71-154

Ylang Ylang oil forms a clear solution with 1–1½ vols. of 90 p.c. alcohol, becoming turbid on further addition of alcohol. Contains methyl and benzyl acetates and benzoates, linalool, geraniol. eugenol, *iso*eugenol, methyl ether of *p*-cresol, methyl salicylate, methyl anthranilate, and an odourless sesquiterpene alcohol melting at 138°. Cadinene is also present. For other commercial varieties the following characters have been recorded :—

—	Reunion oil	Madagascar	Seychelles
Sp gr. . .	0 939 -0 967	0 961–0 981	0 924 0 958
Rotation .	- 30° to 64°	–50°	–18° to –45°
Sapon. No. .	96 98	119	—

C. T. B.

OILS (FIXED) and **FATS.** Oils and fats are distributed throughout the vegetable and animal kingdoms from the lowest organisms up to the most highly organised forms of vegetable and animal life, and are found in almost all tissues and organs. The vegetable oils and fats are deposited in considerable quantities in the seeds, and are associated there with starch, nitrogenous substances, &c., to serve as nourishment to the embryo. Exceptionally, oil has been found in considerable quantities in the rhizomes of *Cyperus esculentus* (Linn.). In the animal organism, oils and fats are mainly enclosed in the cellular tissues of the intestines and in the tissues nearest the outer skin.

The fatty (fixed) oils and fats form a well-defined and homogeneous group of substances, passing through all gradations of consistency, from oils which are fluid even below the freezing-point of water, up to the hardest fats which melt at about 60°. Therefore no sharp distinction can be made between fatty oils and fats. Nevertheless, it is convenient to apply the term 'oil' to those glycerides which are fluid below about 20°, and the term 'fat' to those which are solid above this temperature.

The natural oils and fats may, for practical purposes, be looked upon as consisting in the main of mixtures, in varying proportions, of the triglycerides described under Glycerin.

No natural oil or fat consists of one simple triglyceride, although some of the vegetable fats derived from the *Myristicaceæ* contain very small quantities only of fatty acids other than myristic. The natural oils and fats must rather be looked upon as mixtures or compounds of at least two or three triglycerides, the most important of which would be represented by trilaurin, trimyristin, tripalmitin, tristearin, triolein, trilinolin, trilinolenin, triclupanodonin, and triricinolein. The glycerides of hydnocarpic and chaulmoogric acids are characteristic of the fats of the chaulmoogra group (*q.v.*). Other glycerides occurring in much smaller quantities are glycerides containing butyric acid (in butter fat), caproic, caprylic, capric acids (in butter fat, coconut oil, palm-nut oil), lauric acid (in coconut oil, palm-nut oil, dika fat), and arachidic acid (in arachis oil).

A systematic survey of the most important fatty acids occurring in oils and fats as glycerides is given in the table on p. 647.

In consequence of the discovery of mixed glycerides, the question whether mixed glycerides occur in the natural fats far more frequently than has been assumed hitherto has become a very important one. A good deal of evidence goes to show that the amount of simple triglycerides in such common fats as, *e.g.*, tallow and lard is very small indeed, and that the bulk of the triglycerides consists of mixed glycerides. At present, however, our knowledge is still too limited to justify any definite expression of opinion as to the exact composition of the glycerides in the natural oils and fats (*cf.* also Glycerin).

To sum up, oils and fats must not be looked upon as chemical individuals, but rather as representatives of natural species which vary, although within certain narrow limits, according to the climate and soil in which the plants producing them are grown; or, in the case of animal fats, according to the climate, the race, the age of the animal, and especially the food, and also to some extent the idiosyncrasy of the individual.

Freshly-prepared fats apparently contain only triglycerides, and under normal conditions, monoglycerides and diglycerides do not appear to be present. The occurrence of the diglyceride of erucic acid in a specimen of crude rape oil is due to the fact that that specimen had become rancid, with the formation of lower glycerides than a triglyceride.

Monoglycerides and diglycerides (*see also* Glycerin) have hitherto been obtained only synthetically. As they have not acquired any practical importance, the reader is referred to the list of monoglycerides and diglycerides collated in Lewkowitsch's Chem. Technology.

From the table given on p. 646, it will be gathered that, for practical purposes, a classification of oils and fats can be based on the nature of the fatty acids as measured by their degree of unsaturation. This is best ascertained by determining the magnitude of the iodine absorption of the natural oils and fats, whereby a most important measure of the amount of unsaturated glycerides contained in a given oil or fat, is found. In a classification based on the iodine value the old grouping of oils, other than marine animal oils, into *drying oils*, *semi-drying oils*, and *non-drying* oils is implicitly contained.

The apparently antiquated subdivision into vegetable and animal oils and fats did not rest on a scientific basis, until it had been found possible to differentiate chemically between cholesterol and phytosterol (*q.v.*). All evidence goes to show that cholesterol occurs only in oils and fats of animal origin and is characteristic thereof, whereas phytosterol (sitosterol and its congeners) has been found hitherto only in vegetable oils and fats. Based on these two principles, the author put forward a scheme of classification of the natural oils and fats (Conférence, Bull. Soc. chim. 1909) which is arranged in a synoptic table on p. 646.

The tables, pp. 648–650, furnish a list of the most important oils and fats, arranged according to the classification set out in the foregoing table. There are added the botanical and zoological sources, the proportions of oil or fat contained in the seeds or fruits of the plants, the iodine values of the oils and fats, and their principal uses.

I. VEGETABLE OILS AND FATS.

A. *Vegetable Oils.*

1. Drying oils.
2. Semi-drying oils—
   (*a*) Cottonseed oil group.
   (*b*) Rape oil group.
3. Non-drying oils—
   (*a*) Almond oil group.
   (*b*) Olive oil group.
   (*c*) Castor oil group.

B. *Vegetable Fats.*

1. Chaulmoogra oil group.
2. Laurel oil group.
3. Palm oil group.
4. Myristica group.
5. Cacao butter group
6. Coconut oil group.
7. Dika fat group.

II. ANIMAL OILS AND FATS.

A. *Animal Oils.*

1. Marine animal oils—
   (*a*) Fish oils.
   (*b*) Liver oils.
   (*c*) Blubber oils.
2. Terrestrial animal oils—
   (*a*) Semi-drying oils.
   (*b*) Non-drying oils.

B. *Animal Fats.*

1. Drying fats.
2. Semi-drying fats.
3. Non-drying fats—
   (*a*) Body fats.
   (*b*) Milk fats

The determination of oils and fats in the raw materials of the oil and fat industries is effected in the chemical laboratory by heating the finely divided substance with ether, petroleum ether, or similar solvents. The comminution of hard oil seeds may be effected in a porcelain mortar, which is finally washed out with the solvent so as not to lose any fatty matter which has exuded. It is also feasible to apply an ordinary coffee-grinder, but in this case it is more difficult to avoid loss of fat. In laboratories where such determinations are carried out frequently, special grinding machines are used and loss is obviated by squeezing a large quantity of seeds through the machine. In case the substances contain a considerable amount of moisture, it is best to dry them previously, provided the oil or fat does not suffer an injurious change thereby. If oxidation of the oil or loss of volatile substances is to be expected, the oil or fat may be extracted from the moist substances by means of petroleum spirit boiling below 80°. Ether is most satisfactory for general use, but with this solvent the substance must be dried first. Carbon disulphide and chloroform may also be used, but in this case also it is necessary to dry the substance previous to extraction. The choice of the solvent is by no means immaterial; thus carbon disulphide (which is largely used in France) extracts a larger amount of substances than do ether or petroleum (*cf.* Lewkowitsch, Chem. Technology).

The most convenient apparatus for the extraction of fat is the one devised by Soxhlet (Szombathy) (see Fig. 1). 10–15 grams of the comminuted substance are introduced into a cartridge of filter-paper, easily prepared by rolling filter-paper round a cylindrical piece of wood of suitable size, and folding it up at one end. The cartridge is filled with the substance and transferred to the extractor E. Care must be taken that the siphon tube be not stopped up by the paper case; nor should the cartridge be filled to the top, lest some particles of the substance be washed over by the solvent and carried away. To be quite safe, it will be found advisable to place a plug of (extracted) cotton-wool on the top of the substance, or to close the top by folding the paper over it. The tube N is then fitted by means of a cork to a flask charged with about 50 c.c. of the solvent (petroleum, ether, chloroform, &c.). Another portion of the solvent is carefully poured on to the substance in E, until it commences to run off through the siphon S. Finally, an inverted condenser is fitted to E, and the whole apparatus is placed on a water-bath. In using this form of Soxhlet's extractor there is always some doubt as to the exact time when the extraction is complete, and, as a rule, the operation lasts much longer than necessary, involving both loss of time and solvent. To avoid this, Lewkowitsch has a tap fitted on to the siphon tube, so that some of the solvent can be withdrawn at any time to ascertain the progress of extraction (*see* Fig. 2). If the substance to be extracted has been collected on a filter, the simplest plan is to fold the filter and place it at once in the extractor.

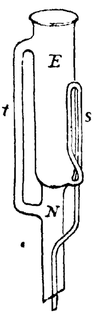


FIG. 1.

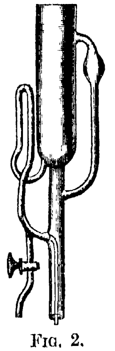


FIG. 2.

When the extraction is complete, the flask containing the solution is detached from the extractor, the solvent is distilled off on the water-bath, and the fat dried in an air-bath at a temperature not exceeding 100°–110°, until the weight remains fairly constant.

In case the substance has not been dried completely, and ether has been used, it is advisable to extract the residue once more with petroleum spirit. The drying of the residue is effected by placing the flask in a drying oven, heating to 100°–105°, and turning the contents round the walls of the flask at frequent intervals. If the minute drops of water which collect at the bottom of the oily layer have disappeared, the drying may be considered to be completed. This must be confirmed by re-weighing after further drying for half an hour. In the case of drying oils, it is best to heat the flask in an oil-bath at the temperature of 100°–105°, while a slow current of carbon dioxide or of hydrogen is allowed to pass over the surface of the oil.

TECHNICAL PREPARATION OF OILS AND FATS.

Rendering.—Since oils and fats have served the human race as one of the most important articles of food, the methods of preparing oils and fats may be considered to date back as

——	Chemical composition	Boiling-point.		Melting-point °C.	Characteristic of
		Under mm. pressure	°C.		
I Acids of the Acetic series, $C_nH_{2n}O_2$—					
Acetic acid	$C_2H_4O_2$	760	119	17	Spindle-tree oil, Macassar oil.
Butyric acid	$C_4H_8O_2$	760	162·3	−6·5	Butter fat, Macassar oil.
*iso*Valeric acid (?)	$C_5H_{10}O_2$	760	173·7	−51	Porpoise and dolphin oils.
Caproic acid	$C_6H_{12}O_2$	770	202–203	−8	Butter fat, coconut oil, palm nut oil.
Caprylic acid	$C_8H_{16}O_2$	671	236–237	16·5	
Capric acid	$C_{10}H_{20}O_2$	760	268–270	31·3	
Lauric acid	$C_{12}H_{24}O_2$	100	225	43·6	Laurel oil, coco-nut oil.
Myristic acid	$C_{14}H_{28}O_2$	100	250·5	53·8	Mace butter, nutmeg butter.
Palmitic acid	$C_{16}H_{32}O_2$	100	271·5	62·61	Palm oil, Japan wax, myrtle wax, lard, tallow, etc.
Stearic acid	$C_{18}H_{36}O_2$	100	291	69·32	Tallow, cacao butter, etc.
Arachidic acid	$C_{20}H_{40}O_2$	—	—	77	Arachis oil.
Behenic acid	$C_{22}H_{44}O_2$	60	306	83–84	Ben oil.
Lignoceric acid	$C_{24}H_{48}O_2$	—	—	80·5	Arachis oil.
II. Acids of the Acrylic or Oleic series, $C_nH_{2n-2}O_2$—					
Tiglic acid.	$C_5H_8O_2$	760	198·5	64·5	Croton oil.
Hypogæic acid	$C_{16}H_{30}O_2$	15	236	33–34	Arachis oil.
Oleic acid	$C_{18}H_{34}O_2$	100	285·5–286	6·5	Most oils and fats.
Rapic acid	$C_{18}H_{34}O_2$	—	—	—	Rape oils.
Erucic acid	$C_{22}H_{42}O_2$	30	281	33–34	Rape oils, fish oils.
III. Acids of the Linolic series, $C_nH_{2n-4}O_2$—					
Linolic acid	$C_{18}H_{32}O_2$	14	228	—	Soya bean oil, Maize oil, cotton-seed oil.
Telfairic acid	$C_{18}H_{32}O_2$	13	220–225	—	Koeme oil.
Elæomargaric acid	$C_{18}H_{32}O_2$	—	—	48	Tung oil.
IV. Acids of the Cyclic (Chaulmoogric) series, $C_nH_{2n-4}O_2$—					
Hydnocarpic acid	$C_{16}H_{28}O_2$	—	—	59–60	Hydnocarpus, lukrabo, and chaulmoogra oils.
Chaulmoogric acid	$C_{18}H_{32}O_2$	20	247–248	68	
V. Acids of the Linolenic series, $C_nH_{2n-6}O_2$—					
Linolenic acid	$C_{18}H_{30}O_2$	—	—	—	Linseed oil.
*iso*Linolenic acid	$C_{18}H_{30}O_2$	—	—	—	
VI. Acids of the Clupanodonic series, $C_nH_{2n-8}O_2$—					
Clupanodonic acid	$C_{18}H_{28}O_2$	—	—	liquid	Fish, liver, and blubber oils.
VII. Acids of the Ricinoleic series (hydroxylated acids, $C_nH_{2n-2}O_3$—					
Ricinoleic acid	$C_{18}H_{34}O_3$	15	250	4–5	Castor oil.
VIII. Dihydroxylated acids of the series $C_nH_{2n}O_4$—					
Dihydroxystearic acid	$C_{18}H_{36}O_4$	—	—	141–143	Castor oil
IX. Acids of the series $C_nH_{2n-2}O_4$ (dibasic acids)—					
Japanic acid	$C_{21}H_{40}O_4$	—	—	117·7–117·9	Japan wax.

I. VEGETABLE OILS AND FATS.

A. Vegetable Oils.

	Oil	Source	Proportion of oil in seed or fruit	Iodine value	Used in the production of
		1. Drying Oils.			
	Perilla	Perilla ocymoides	35·8	206·1	Varnishes.
	Linseed	Linum usitatissimum	38-40	175–205	Paints, varnishes, linoleum, soft soap.
	Tung (*a*) Chinese (*b*) Japanese	Aleurites cordata	53	150–163	Paint and varnish.
	Candle nut	Aleurites moluccana	62-64	163	Burning oil, soap, paint.
	Hemp seed	Cannabis sativa	30-35	148	Paints and varnishes, soft soap.
	Walnut: nut	Juglans regia	63-65	145	Paints.
	Safflower	Carthamus tinctorius	30-32	130–147	Burning oil, varnish ('roghan').
	Poppy seed	Papaver somniferum	41–50	123–143	Salad oil, paints, soft soap.
	Sunflower	Helianthus annuus	21–23	119–135	Edible oil, soap.
	Soya bean	Soja hispida	18	137–141	Edible oil, burning oil, soap.
	Cameline (Ger. Sesamé)	Camelina sativa	31–34	135	Burning oil, soap.
	Madia	Madia sativa	32–33	118·5	Soap, burning oil.
		2. Semi-Drying Oils.			
(*a*) Cotton-seed oil group	Pumpkin seed	Cucurbita pepo	47–48	123–130	Edible oil, burning oil.
	Maize: corn	Zea mais	6–10	113–125	Edible oil, soap.
	Beech nut	Fagus sylvatica	43–45	111–120	Edible oil, burning oil.
	Kapok	Bombax pentandium (Eriodendron anfractuosum)	30 32	116	Edible oil, soap.
	Cotton seed	Gossypium herbaceum	24-26	108–110	Edible oil, soap.
	Sesamé	Sesamum orientale, S. indicum	50-57	103–108	Edible oil, soap.
	Curcas, purging nut	Jatropha curcas	55–57	98–110	Medicine, soap.
(*b*) Rape oil group	Brazil nut	Bertholletia excelsa	73	90–106	Edible oil, soap.
	Croton	Croton tiglium	53–56	102–104	Medicine.
	Ravison	Wild Brassica campestris	33-40	105–117	Lubricants, burning oil.
	Hedge Mustard	Raphanus raphanistrum	35-40	105	
	Rape (colza)	Brassica campestris	33-43	94–102	Lubricant, burning oil.
	Black Mustard	Brassica nigra (Sinapis nigra)	31-33	116·1	Soap.
	White Mustard	Brassica alba (Sinapis alba)	85-86	92–103	Soap.
	Radish seed	Raphanus sativus	45–50	92-112	
	Jamba	Brassica campestris var.	24	95	Burning oil, lubricant.
		3. Non-Drying Oils.			
(*a*) Almond oil group	Cherry kernel	Prunus cerasus	35-36	110–114	Edible oil, burning oil, soap.
	Apricot kernel	Prunus armeniaca	40–45	96–108	Perfumery, medicine.
	Plum kernel	Prunus domestica Prunus damascæna	25		
	Peach kernel	Prunus persica	32–35	93–108	Perfumery, medicine.
	Almond	Prunus amygdalus	45–55	93–100	Perfumery, medicine.
(*b*) Olive oil group	Arachis (groundnut)	Arachis hypogæa	43–45	83–100	Edible oil, soap.
	Hazel nut	Corylus avellana	50–60	83–90	Edible oil, perfumery, lubricant.
	Olive	Olea europæa	40–60	79–88	Edible oil, lubricant, burning oil, soap.
	Olive kernel	Olea europæa	12–15	87	Edible oil, lubricant, burning oil, soap.
	Ben	Moringa oleifera	35-36	82	Edible oil, perfumery, lubricant.
(*c*) Castor oil group	Grape seed	Vitis vinifera	10–20	96	Edible oil, burning oil.
	Castor	Ricinus communis	46–53	83-86	Medicine, soap, Turkey red oil; lubricant.

B. Vegetable Fats.

	Fat	Source	Proportion of oil in seed or fruit	Iodine value	Used in the production of
	Laurel oil group—				
	Laurel oil	Laurus nobilis	24–26	68–80	Medicine.
Palm oil group	Mowrah seed oil	Bassia latifolia Illipe latifolia	50–55	63	Edible fat, soap, candles.
	Mahua butter				
	Mowrah butter	Bassia longifolia	50–55	58–63	Edible fat, soap, candles.
	Illipe butter				
	Macassar oil Kusum oil	Schleichera trijuga	70·5	48–69	Medicine.
	Palm oil	Elæis guineensis, E. melanococca	16–44	53	Candles, soap.
Myristica group	Mace butter Nutmeg butter	Myristica officinalis	38–40	40–52	Medicine, perfumery.
	Phulwara butter	Bassia butyracea	50–52	42	Edible fat.
	Shea butter (Galam butter)	Bassia Parkii	49–52	56	Edible fat, soap, candles.
Cacao butter group	Mkányi fat	Stearodendron Stuhlmannii	67	41·9	Soap, candles.
	Malabar tallow	Vateria indica		37–40	Edible fat.
	Cacao butter	Theobroma cacao	44–50	32–41	Chocolate.
	Chinese vegetable tallow	Stillingia sebifera (Croton seb.)	22	28–32	Soap, candles.
	Kokum butter (Goa butter)	Garcinia indica	49	33	Edible fat.
	Borneo tallow	Shorea stenoptera, Hopea aspera	45–50	15–31	Edible fat, candles.
Coconut oil group	Mocaya oil	Cocos sclerocarpa	60–70	24	Edible fat, soap.
	Maripa fat	Palma (?) maripa	—	17	„ „
	Palm kernel oil	Elæis guineensis E. melanococca	45–50	13–14	
	Palm nut oil				„ „
	Coconut oil	Cocos nucifera, C. butyracea	20–25	8–9	Edible fat, soap, candles.
Dika fat group	Dika oil (oba oil, wild mango oil)	Irvingia gabonensis	60–65	5·2	Edible fat.
	Japan wax	Rhus succedanea, R. vernicifera	25	4–10	Polishes.
	Myrtle wax	Myrica cerifera, M. carolinensis	20–25	2–4	Soap, candles (?).

II. ANIMAL OILS AND FATS.

A. Animal Oils.

Oil	Source	Iodine value	Principal use
	1. Marine Animal Oils.		
(*a*) Fish oils—			
Menhaden	Alosa menhaden	140–173	Currying leather ; soap making.
Sardine	Clupea sardinus	161–193	„ „ „
Japanese sardine	Clupanodon melanosticta	187	„ „ „
Salmon	Salmo salar	161	Currying leather.
Herring	Clupea harengus	124–142	„ „
Stickleback	Gasterosteus trachurus	162	„ „
Sturgeon	Accipenser sturio	125·3	„ „
Sprat	Clupea sprattus, Cuv.	122–142	„ „
(*b*) Liver oils—			
Cod liver	Gadus morrhua	167	Medicine, currying leather.
Skate liver	Squatina vulgaris	157·3	„ „ „
Tunny liver	Thynnus vulgaris	191·1	„ „ „
Shark (Arctic)	Scymnus borealis	115	Currying leather.
Coal fish	Gadus merlangus (virens)	161·1	„ „
Hake liver	Merluccius commun. (vulgaris)	—	„ „
Ray liver	Raja clavata (batis)	—	„ „
Ling liver	Molva vulgaris	132–151	„ „

II. ANIMAL OILS AND FATS—*continued.*

A. Animal Oils.

Oil	Source	Iodine value	Principal use
(*c*) Blubber oils—			
Seal	Phoca vitulina	137–147	Burning, currying leather.
Whale	Balæna mysticetus	121–136	Burning, soap-making, fibre dressing, currying leather.
Dolphin, black fish			
Body oil	Delphinus globiceps	99–126	Lubricating oil for delicate machinery.
Jaw oil		33	
Porpoise—			
Body oil			
Jaw oil	Delphinus phocæna	119	
2. Terrestrial Animal Oils			
Non-drying oils—			
Sheep's foot	Ovis aries	74	Lubricating.
Horses' foot	Equus caballus	74–90	,,
Neat's foot	Bos taurus	67–73	Lubricating, leather.
Egg	Gallus domesticus	68–82	Leather dressing.

B. Animal Fats.

	Fat	Source	Iodine value	Principal use
	1. Drying Fats.			
	Ice bear	Ursus maritimus	147	Pharmacy.
	Rattlesnake	Crotalus durissus	106	,,
	2. Semi-drying Fats.			
	Blackcock	Tetrao urogallus	121·1	
	Hare	Lepus timidus	102·2	
	Rabbit, wild	Lepus cuniculus	99·8	
	Rabbit, tame	Lepus cuniculus	67·6	
	Wild duck	Anas boschas	84·6	
	Domestic duck	Anas boschas	58·5	
	Horses' fat	Equus caballus	75–85	Edible fat, soap.
	3. Non-drying Fats.			
Body fats	Horse marrow fat	Equus caballus	77–81	Food, soap.
	Domestic goose	Anser cinereus		Food.
	Wild goose	Anser ferus	99·6	
	Lard	Sus scrofa	66	Food, soap.
	Hog, wild	Sus scrofa	76·6	
	Beef, marrow	Bos taurus	55	Pomades.
	Bone	Bos; Ovis	46–56	Soap, candles.
	Tallow, beef	Bos taurus	38–46	Food, soap, candles, lubricants.
	Tallow, mutton	Ovis aries	35–46	Food, soap, candles, lubricants.
Milk fat	Butter	Bos taurus	26–38	Food.

far as the history of the human race itself. The crudest methods of 'rendering' oils from seeds and fruits, which are still practised at present in Central Africa, in Indo-China, the Malay Archipelago, and the South Sea Islands, consist in allowing the broken fruits to melt by the heat of the sun, when the exuding oil runs off and is collected. The production of palm oil by the natives, as also of the preparation of best coconut oil by boiling the fruit kernels with water, are more modern developments of this method, which culminates in the *boiling-out method* practised on the largest scale by 'rendering' animal fats and oils from the tissue, as is done in the preparation of tallow, lard, whale oil, cod-liver oil, &c. The most modern practice in the carrying out of this process, as worked in the enormous packing houses (rendering establishments) in America (tallow, lard, bone fat), and in the modern whale oil and fish oil rendering works, consists essentially in cutting up the fatty tissues into small fragments, which are transferred into vessels containing water, wherein the comminuted mass is heated by steam, either under ordinary pressure in open vessels or under higher pressure in digesters. The fat gradually exudes and collects on the top of the water, whilst the membranous matter ('greaves') falls to the bottom. The fat is then drawn off from above the aqueous (gluey) layer, and strained through sieves or filters. The 'greaves' are placed in hair or woollen bags and submitted to hydraulic pressure, whereby a further portion of oil or fat is obtained. In the case of those animal fats which are intended for edible purposes, such as lard or suet for margarine, the greatest cleanliness must, of course, be observed, and the temperature must be kept as low as possible in order to obtain a perfectly 'sweet' and pure material.

Pressing.—The preparation of oils and fats from small oleaginous seeds, such as linseed and rape seed, was practised originally by crushing the seeds and grinding between stones, as is still done in India. A more modern development, still in vogue in Manchuria in the production of soya bean oil, consists in bruising the seeds and reducing them under an edge-stone, heating the meal in an open pan, and pressing out the oil in a wedge-press, the wedges being driven home by hammers. The screw-press used in vineyards served as a model for the construction of the primitive olive-press. The several stages through which the industry of oil presses developed from these early beginnings of machinery to the Dutch wedge-press, until it reached the most complete form of modern oil-pressing plant, cannot be detailed here, and the reader is therefore referred for a rapid survey to Lewkowitsch's Chemical Technology. It must suffice here to state that the most modern presses in vogue at present are the *Marseilles press*, the *Anglo-American press*, and the *cage press* (clodding press), which have reached their present completeness through the combination of the inventions of the hydraulic press by Joseph Bramah (1795), and of the accumulator by William George (later Lord) Armstrong (1843). It is due to the early application of these inventions in this country, that England secured the supremacy in the oil-crushing trade in the latter half of the last century and has been able to retain it, notwithstanding severe foreign competition.

The sequence of operations in treating oil seeds, oil nuts, &c., for the separation of the oils they contain is, at the present time, as follows: As a preliminary operation the oil seeds and nuts are freed from dust, sand, and other impurities by sifting in an inclined revolving cylinder or sieving machine, covered with woven wire, having meshes varying according to the size and nature of the seed operated upon. This preliminary purification is of the greatest importance, especially for the preparation of *edible oils and fats*. In the case of those seeds liable to contain pieces of iron (hammer heads and nails, amongst palm kernels, &c.), the seeds are passed over magnetic separators, which retain the pieces of iron. The seeds and nuts are then decorticated (when required), the shells removed, and the kernels ('meats') converted into a pulpy mass or meal (in older establishments by crushing and grinding between stones in edge-runners) by being passed through a hopper over rollers consisting of (five) chilled-iron or steel cylinders mounted vertically like the bowls of a calendar. These rollers are finely grooved so that the seed is cut up while passing in succession between the first and second rollers in the series, then between the second and the third, and so on to the last, when the grains are sufficiently bruised, crushed, and ground. The distance between the rollers can be easily regulated so that the seed leaving the bottom roller has the desired fineness. The comminuted mass, forming a more or less coarse meal, is either expressed in this state or subjected to a preliminary heating, according to the quality of the product to be manufactured. For the preparation of edible oils and fats the meal is expressed in the cold, after having been packed into bags and placed in hydraulic presses under a pressure of 300 atmospheres or more. The cakes are allowed to remain under pressure for about 7 minutes. The oil exuding in the *cold* dissolves the smallest amount of colouring matter &c., and hence has suffered least in its quality. Oils so obtained are known in commerce as 'cold-drawn oils,' 'cold-pressed oils,' 'salad oils,' 'virgin oils.'

By pressing in the cold, obviously only part of the oil or fat is recovered. A further quantity is obtained by expressing the seed meal at a somewhat high temperature, reached by warming the comminuted seeds or fruits either immediately after they leave the five-roller mill, or after the 'cold-drawn oil' has been taken off. Of course, the cold-pressed cakes must be first disintegrated, which may be done under an edge-runner. The same operation may be repeated once more. Thus oils of the 'second expression' and of the 'third expression' are obtained.

In the case of oleaginous seeds of low value (cotton-seed, linseed) it is of importance to express in one operation the largest possible quantity of oil. Hence, after leaving the five-roller mill, the bruised seed is generally warmed at once in a steam-jacketed kettle fitted with a mixing gear, by passing steam into the jacket, and sending at the same time some steam through a rose, fixed inside the kettle, into the mass while it is being agitated. This practice is a survival of the older method of moistening the seed with a little water, while the seeds were bruised under edge-runners, so as to lower the temperature and facilitate the bursting of the cells. The warm meal is then delivered through measuring boxes into closed press-bags ('scourtins' of the 'Marseilles' press), or through measuring boxes, combined with an automatic moulding machine, into cloths open at two sides (Anglo-American press), so that the preliminary pressed cakes can be put at once into the hydraulic press. In the latest constructions of cage-presses, the use of bags is entirely dispensed with, a measured quantity of seed falling direct into the circular-press cage and being separated from the material forming the next cake by a circular plate of sheet iron.

The method of expressing is exclusively employed wherever the pressed cakes are used as cattle food. These cakes retain a notable amount of oil or fat—from 5 to 10 p.c.—which must, however, not be considered as lost, inasmuch as the fat constitutes a most valuable and, indeed, necessary constituent of cattle food.

Extraction by solvents.—In those cases where the full yield, or approximately full yield, of the oil contained in the seeds is aimed at, the comminuted seeds are extracted with volatile solvents, such as petroleum hydrocarbons, boiling below 120°, and carbon disulphide. As these solvents are highly inflammable, methods of extraction by means of the non-inflammable carbon tetrachloride and chlorine derivatives of ethane (such as dichloro-ethylene $C_2H_2Cl_2$, trichloro-ethylene C_2HCl_3, perchloro-ethylene C_2Cl_4, tetrachloro-ethane $C_2H_2Cl_4$, and pentachloro-ethane C_2HCl_5) have been introduced. At present the high price of these solvents still militates against their general employment, in addition to some other drawbacks in their use.

The apparatus employed on a large scale depends on the temperature at which the extraction is carried out. In the main two types of extracting apparatus may be differentiated, viz. for extraction in the cold and for extraction in the hot. The seed is prepared in a similar manner as for pressing, except that it is not reduced to a fine meal, so as not to impede the percolation of the solvent through the mass. In the case of *cold extraction* the seed is placed in a series of closed vessels, through which the solvent percolates by displacement, on the 'counter-current' system. A battery of vessels is so arranged that one vessel can always be made the last of the series to discharge finished meal and to be recharged with fresh meal, so that the process is practically a continuous one. The solution of the extracted oil or fat is then transferred to a steam-heated still, where the solvent is driven off and recovered by condensing the vapours in a cooling coil, to be used again. The last remnant of volatile solvent in the oil is expelled by a current of open steam blown through the oil in the warm state. The extracting process *in the hot* is carried out in an apparatus, the principle of which is exemplified by the well-known Soxhlet extractor. The comminuted seed is placed on trays or baskets inside a vessel connected with an upright refrigerator, and is surrounded there by the volatile solvent. On heating the solvent with steam through a coil or jacket, the vapours rise through and around the meal. They pass into the refrigerator, where they are condensed and fall back as a liquid through the meal, percolating it on their way downwards, and reaching the bottom of the vessel as a more or less saturated solution of oil in the solvent. The solvent is again evaporated, leaving the oil at the bottom of the vessel until the extraction is deemed finished. The solution of fat is then run off into a still, as described already, and the last traces of solvent are driven out. The solvent is recovered and used again.

The meal left after extraction is not suitable for cattle food, and no extracted meal can be sold in this country for feeding purposes. On the Continent, however, frequent endeavours are being made to sell (and even recommend under specious 'scientific' pretensions) extracted meal for feeding purposes, and although Agricultural Associations in many cases stipulate that no extracted meal should be accepted by farmers, yet a considerable amount of extracted meal finds its way, chiefly on the Continent, into 'compound cakes.'

With regard to the merits and demerits of the last two mentioned processes—expression and extraction—the adoption of either must largely depend on local conditions and the objects for which the products are intended. Wherever the cake is the main product, expression will commend itself as the most advantageous process. Where, however, the fatty material forms the main product, as in the case of palm kernel oil, or sesamé and coconut oils from damaged seeds (which would no longer form proper cattle food), the process of extraction will be preferred, especially when the price of oil is high. In some cases the combination of the two processes commends itself, as in the production of olive oil. The fruits are expressed, and after the edible qualities and best classes of oils for technical purposes have been taken off by expression, the remaining pulp is extracted by means of solvents. This process is known under the name of the mixed process (*huilerie mixte*) [*v.* OLIVE OIL].

Refining and *bleaching*.—The oils and fats prepared by any of the methods described above are, if obtained from perfectly fresh ('sweet') material, and in their fresh state, practically neutral. If care be exercised in the process of rendering animal oils and fats, or expressing vegetable oils in the cold, the products are, as a rule, sufficiently pure to be delivered to the consumer, after a preliminary settling has allowed any mucilaginous matter, such as animal or vegetable fibres or other impurities, as also traces of moisture, to separate out. This spontaneous clarification was at one time the only method in vogue. This process is now shortened by filtering oils through filter presses, or otherwise 'brightening' them, *e.g.* by blowing with air. In many cases these methods still suffice for the production of commercial oils and fats.

In special cases, such as the preparation of edible oils and fats, a further improvement in colour, and at the same time greater purity is obtained by filtering the oils over charcoal, or over natural absorbent earths, such as fuller's earth. Where this process does not suffice, as in the case of coconut oil or palm kernel oil, a preliminary purification in a current of steam must be resorted to before the final purification, described above, is carried out.

Oils, intended for table use, which deposit 'stearine' in winter, must be freed from such solid fats. This is done by allowing the oil to cool down to a low temperature and pressing the cold oil through the cloths in a press, when a limpid oil exudes, which remains proof against cold. Such oil is termed 'winter oil.' Thus whereas most olive oils are naturally non-congealing oils, the Tunisian and Algerian olive oils deposit so much 'stearine' that they must be 'demargarinated.' Similar methods are employed in the production of lard oil, edible cotton-seed oil, &c.

For *refining* oils and fats intended for edible purposes only the foregoing methods, which may be summarised under the name of *physical methods*, can be used; the only chemicals permissible are alkalis or alkaline earths to remove any free fatty acids present. Treatment with other chemicals renders the oils and fats unfit for consumption. Therefore all bleaching and refining processes involving other means than those enumerated can only be employed for oils and fats intended for technical purposes, such as lubricating oils, burning oils, paint oils, soap-making oils, &c.

Bleaching with the aid of chemicals requires great circumspection. There is no universal method of oil-refining applicable to any and every oil or fat. Not only must each kind of oil or fat be considered as a special problem, but frequently even varieties of one and the same oil or fat are apt to cause the same difficulties as would a new individual. In many cases purification by means of sulphuric acid, invented and patented by Charles Gower in 1792 (frequently ascribed to Thénard), is still usefully applied. It consists in treating the oil with a small percentage of a more or less concentrated sulphuric acid, according to the nature of the oil or fat. The acid not only takes up water, but it acts on the suspended impurities, carbonising them to some extent, and thus causing them to coagulate and fall down in the form of a flocculent mass, which carries with it mechanically other impurities which have not been acted upon. This method is chiefly used in the refining of linseed and rape oils.

Purification by means of strong caustic soda was first recommended as a general process by Louis C. Arthur Barreswil, his suggestion being to heat the oil and add 2–3 p.c. of caustic soda. In most cases the purification consisted in removing the free fatty acids from rancid oils and fats, the caustic soda forming a soap with the fatty acids, which would either rise as a scum and lift up impurities with it, or fall to the bottom and carry them down. This process is a useful one in the case of cotton-seed oil. As a rule, however, it is very precarious, since emulsions are formed which in many cases altogether prevent the separation of oil. After the treatment with sulphuric acid or caustic soda, the oils must be washed to remove the last traces of chemicals. The water is then allowed to settle out, and the oils are finally filtered.

The number of chemicals which have been proposed from time to time for the purification of oils and fats is almost legion, and so long as the nature of oils and fats was little understood, a secret trade in oil-purifying chemicals flourished. With our present knowledge most of these chemicals may be removed into the limbo of useless things.

The general methods of bleaching, besides those mentioned already as physical methods (viz. filtration over charcoal or absorbent earth), are chiefly methods based on treatment with oxygen or with chlorine. The methods of bleaching by oxygen include all those which aim at the bleaching by exposure to the air and to sunlight (as in the case of artists' linseed oil), or where oxygen or ozone is introduced in the form of gas or is evolved by chemicals, such as manganese dioxide, potassium dichromate, or potassium permanganate and sulphuric acid. In the process of bleaching by means of chlorine either bleaching powder or dichromates and hydrochloric acid are used. It must again be emphasised that no general rule can be laid down as to which process should be employed in each given case. There is still a wide field open for the application of proper processes for the removal of impurities and colouring matters without, however, running the risk of attacking the oil or fat itself.

Hence the attention of inventors has been directed during the last few years to the exploitation of this subject and a considerable number of processes and chemicals have been suggested. Thus bleaching by means of ultra-violet rays has, through the introduction of the 'uviol lamp,' gained favour and the bleaching of linseed oil by these means has been patented. It is stated that other oils also can be bleached with the aid of ultra-violet rays ('uviol oils').

Peroxides (sodium peroxide, calcium peroxide, and barium peroxide), persalts (such as perborates, persulphates, percarbonates of sodium or potassium), organic peroxides (benzoyl peroxide, acetyl peroxide, acetone peroxide); further, sodium and calcium hydrosulphites, basic zinc formaldehyde-sulphoxylate and other similar preparations have been suggested and have also been used in practice occasionally. Most of these strongly acting chemicals produce a temporary effect, but frequently the colour 'reverts.' In other cases they introduce such complications into the routine of the oil refiners and of soap and candle manufacturers that it is impossible to recommend them without very serious qualification.

Even after such purification as has been described above, small quantities of non-glyceridic substances remain dissolved. Some of these must be considered as entirely foreign (adventitious) substances, *e.g.* traces of colouring matters, chromogenetic substances (producing the colour reactions which are characteristic of some oils and fats), essential oils, resinous matters, sulphur compounds, and cyanogenetic glucosides.

Other substances are constant concomitants of the natural products, and must therefore be looked upon, to some extent at least, as constituents thereof. The most important of these are phytosterol and cholesterol, inasmuch as the presence or the absence of one or other enables us to recognise a specimen as a vegetable or animal oil or fat. Of less importance are aliphatic alcohols (such as myricyl or ceryl alcohol) and lecithin, although the latter is of very great importance from a physiological point of view (*see* GLYCERIN).

Hydrocarbons, which have been hitherto considered as of little importance, occur more frequently in natural oils and fats than has been ascertained hitherto. More attention is now being paid to their occurrence, as they will probably furnish a means of identifying individual oils and fats.

In their liquid state oils and fats penetrate easily into the pores of dry substances; if dropped on paper they leave a translucent spot—grease spot—which cannot be removed by washing with water and subsequent drying (difference from glycerol spots).

A curious effect, caused by the presence of the minutest quantities of oils and fats, has been described by Lightfoot. Camphor, crushed between layers of paper without having been touched with the fingers, rotates when thrown on to water, but a trace of oil or fat on the surface of the water causes the rotation to cease immediately; it is sufficient to touch the water with a needle which has been passed previously through the hair.

The *specific gravity* of oils and fats varies between the limits 0·910 and 0·976 at 15·5°. The specific gravity alone only exceptionally furnishes a means of identifying an individual oil. Hence the 'oleometers' which were formerly credited with the power of detecting individual oils are now practically abandoned. Castor oil alone can be identified by its exceptionally high specific gravity.

The *solidifying point* of those oils which are fluid at the ordinary temperature ranges from a few degrees above zero down to - 28°C. (linseed oil). (For melting and solidifying points of individual oils and fats, *cf.* tables at the end of this article.)

Although at first sight little importance should be ascribed to the melting and solidifying points, inasmuch as from some oils there separate out on standing glycerides containing solid acids (in practice frequently termed 'stearine' or 'margarine'), they are, from a technical point of view, of importance, as they are a measure of the consistence and furnish reliable guidance in the preparation of 'demargarinated edible oils' or 'racked' fish and cod-liver oils. For the manufacture of such demargarinated oils, the natural oils are exposed to a low temperature. The solid glycerides then separate out as a deposit, and the clear limpid oil can be drawn off as an upper layer after sufficient time has been allowed for subsidence. When the solid glycerides separate out in a crystalline form, this slow and cumbersome process can be shortened by cooling (refrigerating) the oils artificially and filtering the liquid portion from the solid at a low temperature. The limpid oils thus obtained are sold in commerce as 'winter oils.'

Demargarinating is employed on a large scale in the case of cotton-seed oil, whale oil, tallow, and some Algerian and Tunisian olive oils.

The *refractive index* of the natural oils and fats varies within certain limits which, though narrow, are sufficiently characteristic, if observed through accurate optical instruments, to allow a differentiation of the individual oils and fats to a certain extent. This will be further explained below under *Analysis*, but it may be pointed out here that exaggerated importance has frequently been attached to the interpretation of the results of refractometric observation.

Most oils and fats have practically no action on the *plane of polarised light*, the small deviations observed in sensitive polariscopes being chiefly due to adventitious substances, such as cholesterol or phytosterol or resinous or volatile ethereal substances, as in the case of sesamé oil, coconut oil, cod-liver oil.

There are, however, several oils which are distinguished by notable rotations; this is more particularly the case with the oils belonging to the Chaulmoogra group, and it is thus possible by means of the polariscope alone to identify an oil as belonging to this class, as has been done by the author in the case of 'cardamom fat' (*see Chaulmoogra oil group*). Notable rotations are also shown by castor oil and stillingia oil.

Solubility.—Natural oils and fats may be considered as practically insoluble in pure water. On shaking vigorously with large quantities of water, however, minute quantities are dissolved, as is proved by the result of allowing the emulsions formed at first to become clear by standing and shaking out the clear aqueous layer with ether.

On the other hand, oils and fats dissolve small quantities of water, which can be expelled by warming at 100°. From the foregoing it follows that the emulsifying power of water as regards oils and fats is practically *nil*. It can, however, be increased to a very notable extent by addition of small quantities of soap and a number of other substances (*see* Lewkowitsch, Chem. Tech.: *Emulsified Oils and Fats*).

With the exception of castor oil, oils and fats dissolve but very sparingly in *cold alcohol*. Boiling alcohol, however, dissolves somewhat larger quantities, especially of those oils and fats which contain glycerides of the lower fatty acids; but on cooling, nearly all the dissolved substance separates out. The solubility is considerably increased by the presence of free fatty acids; if the amount of the latter be large, exceeding about 30 p.c., even cold alcohol will readily effect solution.

Oils and fats dissolve very readily in ether, carbon disulphide, chloroform, carbon tetrachloride, trichloroethylene (and its congeners), benzene, paraffin oils, and petroleum spirit. Castor oil, however, forms an exception as regards the two last-mentioned solvents. Triacetin is insoluble in carbon disulphide and in petroleum spirit.

Oils and fats dissolve *sulphur* and *phosphorus* at the ordinary temperature to a slight extent. Certain pharmaceutical preparations, notably phosphorised oils, are thus prepared.

The *smell* and *taste* of oils and fats, although frequently characteristic of the individual oils and fats, is due to the presence of certain foreign matters. Thus in the case of fats belonging to the Myristica group the presence of an essential oil imparts the taste of mace. In the case of coconut oil the peculiar taste appears to be due to the presence of some ethereal ketones (occurring also in the essential oil of rue). It may be accepted that in their purified state oils and fats are entirely devoid of free fatty acids, and are practically odourless and tasteless. Hence absolutely neutral oils have an insipid taste.

When freshly rendered, animal fats contain only very small quantities of *free fatty acids*. Oils and fats of vegetable origin, however, even in their fresh state, contain appreciable amounts of free fatty acids. This may be due to the fact that in all seeds there are present enzymes which hydrolyse glycerides, the acid necessary for inducing the hydrolysis being supplied in the form of carbonic acid, which is always present in seeds.

Speaking generally, oils and fats do not suffer any loss when heated at temperatures of 150°–180°. However, oils and fats containing notable quantities of free volatile fatty acids, such as rancid butter fat, and coconut oil, lose in weight, no doubt through volatilisation of free fatty acids; it is not certain that glycerides of the lower fatty acids volatilise as well.

Provided prolonged contact with air is avoided, most oils and fats can be heated to a temperature of about 250° without undergoing a chemical change. (Some oils and fats become paler in consequence of the destruction of dissolving colouring matters, *e.g.* linseed oil.) On being heated above 250°, up to 300°, some oils, especially the drying oils, undergo a change which may be described as due to polymerisation. Thus linseed oil is converted into a thick oil, having a considerably higher specific gravity than that of ordinary linseed oil (*cf.* LINSEED OIL). On this reaction is based the manufacture of *Polymerised Oils.* '*Linseed oil* is converted by heating above 250° into 'varnishes' (not to be confounded with oil-varnishes containing linseed oil, gums, and oil of turpentine), which, according to their specific gravity, are graded in commerce as 'thin varnish' (sp.gr. 0·966), 'medium varnish' (sp.gr. 0·972), 'strong varnish' (sp.gr. 0·974), 'extra strong varnish' (sp.gr. 0·978). These oils find application in lithographic printing and in the preparation of printer's ink, also as 'bird-lime,' and in the manufacture of plastic masses. Hence these oils are known in the trade as '*lithographic varnishes.*' *Tung oil* is converted by heating to 250° into a jelly-like mass, 'polymerised tung oil,' used in the preparation of oil varnishes and even in the manufacture of linoleum. *Polymerised Safflower oil* is prepared in a similar manner from safflower oil. In India this product has been prepared by the natives for many centuries, and is known as 'Roghan' ('Afridi wax'). *Castor oil* especially lends itself to the preparation of polymerised oil, owing to the chemical constitution of *ricinoleic acid* (of which it contains considerable quantities), by prolonged heating, as is practised, *e.g.* in the preparation of cognac oil, when a spongy, very bulky india-rubber-like mass is obtained (for which a solvent has not yet been found). The polymerisation can be accelerated in some cases by the addition of 'condensing agents,' such as concentrated sulphuric acid, aluminium chloride, and zinc chloride.

When oils and fats are heated beyond 250°, decomposition sets in, with the formation of volatile products, the most prominent of which is *acrolein.* The intense odour of acrolein, which all fats emit when heated above 300°, is one of the most characteristic reactions, enabling one to distinguish rapidly fatty oils and fats from mineral and essential oils. Among the volatile products obtained on heating oils and fats to high temperatures are found, besides volatile acids and sebacic acid, hydrocarbons of the ethane, ethylene, and aromatic series (and perhaps also naphthenes), the quantity of which is considerably increased when the destructive distillation takes place under pressure. This fact lends strong support to the theory that the natural petroleum hydrocarbons owe their origin to the destruction of oils and fats. The vegetable fats generally offer much greater resistance to their conversion into hydrocarbons under pressure than do animal oils and fats. If an optically active fat is distilled destructively, the hydrocarbons formed exhibit optical activity (Lewkowitsch, Ber. 1907, 4161). Before gas-making from coal was generally adopted, illuminating gas was frequently prepared from fatty oils. In this connection it may be interesting to remember that Faraday discovered benzene in condensed gas made from whale oil.

As these changes are most important, special attention must be paid to the influence which *light, air,* and *moisture* exert, both separately and conjointly.

Effect of light.—The action of light alone, air and moisture being excluded, has hitherto not been studied thoroughly. It is well known that oils and fats acquire a paler colour under the influence of insolation, some oils even becoming colourless. The application of insolation to industrial purposes is well exemplified by the method of bleaching linseed oil, cod-liver oil, and olive oil under glass or in glass bottles. Since pure glycerides are themselves colourless, the light can only affect the foreign substances dissolved in them. This is further proved by the fact that insolated cotton-seed oil does not reduce silver nitrate so readily as does cotton-seed oil kept in the dark, and that exposure to light destroys those minute traces of chromogenetic substances which give rise to colour reactions that have for a long time been erroneously considered as characteristic (*v. infra*). It would appear that the specific action of light is due especially to the ultra-violet rays (*see* above under *Bleaching*).

Effect of air.—When studying the effect of air we must clearly discriminate between the influence of the ordinary atmosphere—which necessarily includes the action of oxygen, moisture, and light (diffused daylight, direct sunlight)—and the influence of *dry* air, to the exclusion of moisture and light. The effect of the atmosphere on oils and fats varies in a very marked degree with the chemical composition of the glycerides. As a general rule, it may be stated that the greater the proportion of unsaturated fatty acids in the glycerides of oils and fats, the greater is their power to absorb oxygen. The chemical change is most marked in the case of drying oils; it becomes gradually less pronounced with the decrease of the power of absorbing iodine, as we pass through the classes of semi-drying oils and non-drying oils down to the solid fats. Marine animal oils occupy a position similar to that of drying oils. The oxygen absorption power of the various oils and fats will be considered below in the section *Analysis.* Drying oils thicken at first and form an elastic skin on the surface. If exposed in sufficiently thin layers, as, for instance, if spread on wood or glass, they are finally converted into a transparent, yellowish, flexible substance, insoluble in water, alcohol, and also, to a very great extent, in ether (*cf.* LINSEED OIL). While this energetic oxidation takes place, heat is developed to such a degree that if the drying takes place in presence of organic substances in a fine state of division, offering a large surface to the atmosphere (cotton waste, woollen rags), spontaneous combustion will ensue. The non-drying oils remain more or less unchanged. The semi-drying oils occupy an intermediate position. The gradations between the various classes are, however, by no means so distinct as to warrant the drawing of hard and fast dividing lines between the three classes.

The action of air is intensified by spreading oils and fats over finely divided metals (lead powder, copper powder), the metals acting as accelerators or catalysts. This reaction is used for analytical purposes in the determination of the oxygen absorption power of oils (*v. infra*).

Dry air, to the exclusion of moisture and light, has no action on oils and fats, at the ordinary temperature. They will therefore remain unchanged for practically an indefinite length of time, if kept protected from moisture and light. Since it is very difficult to exclude the last traces of moisture when storing oils and fats, such moisture as gains access to the oils and fats will exercise a slight action in the manner described in the following paragraph, that is to say, small amounts of fatty acids will be formed, but rancidity need not set in.

Effect of moisture.—The effect of moisture (always present in the atmosphere) is a far-reaching one. In order fully to understand its effect, it is necessary to consider the action of water on oils and fats.

At temperatures up to about 150° water does not attack glycerides, but if the temperature be raised to 200° or more, the triglycerides are finally decomposed (hydrolysed) into their proximate components, glycerol and fatty acids, whilst the elements of water are assimilated. This action appears to have been observed first by Appert in 1823.

The hydrolysis thus produced at high temperatures is greatly accelerated if the action of the water is assisted by suitable chemical agents (catalysts). If such agents are present, it is possible to reduce the temperature. Thus, by the assistance of concentrated sulphuric acid, the chemical change may be effected at a temperature of about 120°. The temperature required for the chemical change may be further reduced to about 100° by employing strong hydrochloric acid. A still further reduction of temperature can be effected by the introduction of strong bases in alcoholic solution (*see Saponification*). Finally, the change may be brought about by water even at the ordinary temperature, if naturally occurring enzymes, such as lipase, or steapsin, are intimately intermixed with the oils and fats. Fat-hydrolysing enzymes seem to occur in most, if not in all, oleaginous seeds, and no doubt play an important part in the utilisation of the fatty reserve products stored in the seeds. During the germination of the seeds, hydrolysis takes place, and free fatty acids are liberated; hence, it appears very likely that the presence of small quantities of free fatty acids, which are always found in even the freshest vegetable oils and fats, is due to the slight action of these enzymes on the glycerides stored in the seeds. The absence of suitable conditions in ungerminated seeds would appear to lead to limiting very sensibly the progress of hydrolysis. Such conditions are the presence of sufficient water and of small amounts of a mineral acid (carbonic acid, *v. supra*), or of a strong fatty acid (such as acetic acid). If water acidified with small quantities of such acids be churned up with oils and fats, and suitable enzymes be introduced into the mixture, hydrolysis of the glycerides takes place gradually at first, but rises, at the optimum temperature, to a considerable extent within a comparatively short time (*see Saponification*). Thus the ferment contained in castor seed is capable of effecting practically complete hydrolysis in the course of a few days. Enzymes of a similar kind, such as 'catalase, may reasonably be assumed to be contained in commercial animal fats to a smaller or greater extent, according to the care exercised in the separation of the animal tissue from the rendered fat.

Accepting, then, as a fact the occurrence of small quantities of fat-hydrolysing enzymes in those commercial oils and fats which have not been heated to such temperatures that inhibition of the enzymic action must set in, we shall be able to understand those changes which oils and fats undergo on exposure to the atmosphere. As is well known, they acquire thereby a disagreeable smell and an acrid taste; and the presence of free, non-volatile fatty acids, as also of small quantities of volatile acids, may be observed. We comprise these changes under the term 'rancidity,' and we express this by stating that the oils and fats have become 'rancid.'

The effect of light, air, and moisture may now be explained as follows: In the presence of sufficient moisture and acid, enzymes are enabled to accelerate hydrolysis so that a certain proportion of the glycerides may give rise to the production of diglycerides (and monoglycerides) and free fatty acids within a comparatively short time (a few days or a few weeks according to the conditions). Hence the first postulate is that free fatty acids should make their appearance.

It is well known that oils and fats, if kept fully protected from light, air, and moisture, retain indefinitely their state of neutrality, whereas if they are not carefully preserved, moist air easily gains access (as in imperfectly corked bottles, barrels, &c.), and free fatty acids, of the same composition as those which are combined with glycerol in the neutral fat, are produced. The quantity of enzymes in filtered commercial oils and fats being very small, the amount of hydrolysis effected in such oils and fats will be restricted; hence the proportion of free fatty acids in commercial oils and fats does not, as a rule, exceed a few per cent. If, however, oils and fats be allowed to remain in contact with the organic matter from which they have been obtained, such as the marc of fruits (as in the case of olive oil, palm oil, and coconut oil), or animal tissues (as in the case of 'rough fat,' blubber, fish livers), or casein, &c. (as in the case of butter), the hydrolysis of the glycerides increases somewhat rapidly and may reach very high proportions. Thus the so-called bagasse olive oils (*i.e.* oils expressed from exposed olive marc, contain as much as 70 p.c. of free fatty acids. Palm oil may even undergo complete hydrolysis, and hence be found to consist almost exclusively of fatty acids. In all these cases we can satisfactorily explain the formation of a high proportion of fatty acids by the conjoint action of water and enzymes. It appears, therefore, unnecessary to invoke the action of air and light in order to explain the presence of free fatty acids.

The author, therefore, ascribes the primary cause of rancidity, namely, the formation of free fatty acids, to the action of moisture in the presence of soluble enzymes which act as catalysts or accelerators. The occurrence of small quantities of free fatty acids even in refined oils and fats (edible oils and fats), would thus be explained. Yet these oils and fats are by no means rancid. Indeed, the presence of the free fatty acids imparts a slight, not unpleasant, flavour; for it is well known that completely neutral oils and fats have an insipid taste.

Hence, rancidity is not due, as is still widely believed, to the presence of free fatty acids alone; in other words, rancidity must not be considered as coterminous with acidity. The frequent confounding of these two terms is caused by the fact that acid oils and fats are frequently rancid as well. It is only when oxygen and light gain access to the acid fats that the conditions favouring the setting in of rancidity are provided. Rancidity is rather due to the direct oxidation of free fatty acids by the oxygen of the air, assisted and intensified by the exposure to light. Oxygen and light must act simultaneously, either of these agents alone being unable to produce rancidity; hence, the greater the surface offered to the atmosphere the more rapidly will they be able to exercise their influence.

Oils (liquid fats) turn rancid more readily than solid fats. This agrees with the fact that liquid fats are much more easily hydrolysed in the enzymic process (*see Saponification*) than are solid fats, such as tallow. Whether fats containing glycerides of the lower fatty acids (butter fat, coconut oil) are more liable to become rancid than the fats containing glycerides of the higher fatty acids (cacao butter, tallow, &c.) has not yet been decided experimentally. It may, however, be taken as a general rule, that the higher the proportion of insoluble saturated fatty acids, and the lower the percentage of unsaturated glycerides in the fat, the less will be its liability to turn rancid. This rule, however, appears to break down in the case of coconut oil and of Japan wax, which differ greatly in the composition of their constituent glycerides.

Whilst, then, there appears to be no doubt but that rancidity is due to the simultaneous action of moisture, oxygen, and light, very little is known as to the actual chemical change which the liberated free fatty acids undergo. The observation that rancid fats contain free fatty acids had been made before 1814, and both steam distillation and extraction with alcohol were proposed for their removal. The opinion has also been frequently expressed that the bodies characteristic of rancid fats are aldehydes (œnanthaldehyde) and similar substances. Hence the usual reagents employed for the detection of aldehydes have been suggested as a chemical means of differentiating rancid fats from acid fats.

A method of ascertaining the presence of incipient rancidity has been based by Issoglio (Annali Chim. Appl. 1917, 7, 187) on the 'oxidisability value' of the volatile constituents of the fat by means of standard permanganate solution.

Some isolated observations regarding the chemical changes undergone by rancid fats are given in a table, published by Lewkowitsch (Analyst, 1899, 327).

Action of oxygen.—If air, or better still oxygen, be blown through fatty oils at the temperature of boiling water, oxidation takes place. So much heat is thereby evolved that the oxidation process continues without further heating. On this reaction is based the industry of 'blown oils.'

Blown Oils.

The most notable change produced by the action of oxygen is an increase in density (hence they are also termed 'thickened oils'). The oils thus obtained resemble castor oil in their density and viscosity, but differ from it in that they are soluble in petroleum spirit. Hence, these oils are known in the trade also as 'soluble castor oils.' The similarity to castor oil, as also the high acetyl values of the blown oils, has led to the opinion that glycerides of hydroxylated acids are formed, but the fatty acids actually produced differ from the castor oil fatty acids and form a special class of fatty acids, comprised by the author under the term 'oxidised acids.' Fatty oils belonging to the class of semi-drying oils lend themselves specially to the manufacture of 'blown oils.' Thus in commerce there are obtainable: blown maize oil, blown cotton-seed oil, blown rape oil, and blown castor oil. The specific gravity of these oils is increased by the formation of oxidised acids and may reach, according to the time of treatment with air, as high values as 0·96 and above. The chemistry of oxidised oils has been investigated by Lewkowitsch (*see* Chem. Tech. [iii.]). Blown oils are also prepared from fish liver and blubber oils, and are used in the leather industries as also in the production of compound lubricating oils. In the case of drying oils the oxidation process proceeds much further, finally yielding jelly-like or even solid elastic masses. Thus linseed oil dries on exposure to the atmosphere in a thin film to an elastic, thin skin. Blown soya-bean oil also yields a viscous somewhat elastic mass.

Boiled Oils.

Extensive use is made of this action in the industries of boiled oils, paint oils, and varnishes. The boiled oils were up to a few decades ago prepared exclusively by 'heating' linseed oil, as also other drying oils, with a small quantity of suitable metallic oxides or metallic salts—driers, siccatives (*see* DRIERS and LINSEED OIL)—over free fire to temperatures varying from 210° to 260°.

It has been found that linseed oil, after heating with lead oxide, absorbed oxygen more rapidly than did linseed oil not so prepared, and whereas raw linseed oil requires about 3 days for drying to an elastic skin, the drying process is so much accelerated by the treatment with lead oxide over free fire, that linseed oil so prepared will dry even within 6–8 hours to an elastic skin.

What reaction takes place during the process of boiling is not yet fully known. A slight decomposition of the glycerides undoubtedly occurs, as is proved by the evolution of acrolein vapours during the boiling; but such decomposition of the linseed oil is very limited, as the 'boiled oil,' like the polymerised linseed oils (lithographic varnish), still yields almost its full amount of glycerol. Moreover, practical experience has proved that boiled oils must be made from glycerides, since 'boiled oils' cannot be obtained from linseed-oil fatty acids, or from ethyl esters of the mixed linseed-oil fatty acids.

The process of boiling with 'driers' appears to be an empirical way of producing metal salts (lead salts, cerium salts, or manganese salts) of the fatty acids of the boiled oils, partial saponification of the glycerides taking place at the high temperature to which the oils were subjected while being 'boiled.' These lead (or manganese) salts of the fatty acids are able to act as oxygen carriers in the process of 'drying,' when the boiled oils are exposed to the atmosphere either in their original state or in admixture with pigments, gum-resins, &c. This would lead to the explanation that the driers act as catalysts, a small quantity only being required to accelerate the oxidation, so that the oils finally yield a skin. These views find support in the modern methods of preparing 'boiled oils.'

Thus at present the bulk of the 'boiled oils' is obtained by heating linseed oil with driers to a temperature of about 150° only. The process is carried out by introducing the oil into a cylindrical vessel provided with a heating coil and agitating gear, so as to produce an intimate intermixture between oil and drier, while they are heated to the desired temperature.

According to the quality and the amount of drier added, and the length of time during which the oil is heated ('boiled'), *pale* or *dark* oils are produced. The former are known in commerce as 'pale-boiled oils,' the latter as 'double-boiled oils.' The temperature can be reduced even to 120° by merely dissolving 'liquid driers' (solutions of lead linoleate, &c., in linseed oil), and assisting the operation, if required, by a current of air.

These boiled oils have the property of absorbing oxygen from the air at a much more rapid rate than does raw linseed oil, and the time required for the formation of a skin is thereby much shortened.

The chemical change which takes place when a vegetable oil 'dries' to a solid elastic skin, is but very imperfectly understood. The final product appears, however, to be the same, whether raw linseed oil be allowed to absorb oxygen from the atmosphere slowly, or whether the 'drying' be accelerated by previously converting the oil into 'boiled' oil, or the raw linseed oil be treated in a current of oxygen or ozone at a somewhat elevated temperature, after having been intermixed with driers. Mulder's opinion, that in the first stage the glyceridic constituent of the oil is oxidised and that the liberated fatty acids take up oxygen and are converted into the anhydride of 'hydroxylinoleic' acid (*i.e.* the anhydride of hydroxylated linseed oil fatty acids), a neutral substance, insoluble in ether, termed by him 'linoxyn,' must be rejected as erroneous, for this view postulates that hydrolysis of the glycerides precedes oxidation. It has been pointed out already that the solid skin is not formed when the mixed fatty acids are exposed to the atmosphere. Moreover, Bauer and Hazura have shown that, at any rate in the first stage of oxidation, the glyceridic constituent of the linseed oil remains intact, and that the oil is converted by exposure in thin layers into a substance resembling in its properties Mulder's 'linoxyn,' but still representing a glyceride. This substance was assumed by Bauer and Hazura to be hydroxylinolein (*i.e.* a mixture of hydroxylinolin and hydroxylinolenin).

Fahrion has applied Engler and Weissberg's autoxidation theory to this problem, and in the light of this theory he regards the linseed oil as an 'acceptor,' and the driers, especially lead and manganese, which are readily converted into peroxides, as autoxidisers or catalysers. He further argues that some facts seem to show that the drying process may also be considered as a molecular autoxycatalysis, and that driers can therefore only be looked upon as pseudo-catalysers (pseudo-autoxidisers), they causing the addition of hydroxyl groups, and leading to the formation of a secondary autoxidiser. The latter in its turn would take up oxygen in its molecular form, and become converted into a hydroperoxide of a metal and hydrogen peroxide (*cf.* LINSEED OIL).

Genthe, in an elaborate physico-chemical study of the drying of linseed oil, has shown by a series of experiments that the drying process would appear to represent a special case of autocatalysis, inasmuch as his results correspond approximately to numbers obtained by means of the equation $dx/dt = k(m+x)\,(a-x)$ (the equation propounded by Ostwald for auto-catalytic reactions). The substance which acts as the auto-catalyst could, however, not be isolated, and the assumption is made that it has the character of a peroxide. The so-called 'blown boiled oils' would, therefore, be linseed oils, in which peroxides are pre-formed, and the accelerating action which old oil of turpentine possesses would be due to the high proportion of peroxide it contains. (It must, however, not be overlooked, that the peroxide has not yet been isolated.) The 'driers' would thus have to be considered as pseudo-catalysts, their function being to accelerate the drying process by assisting in the formation of autocatalysers ('peroxides').

Boiled oils are not (yet) oxidised oils, but do become oxidised when exposed to the atmosphere, forming the well-known skin which paints (that is intimate mixtures of boiled oil and pigments) form on the painted objects.

The oxidation of linseed oil may be much accelerated by blowing linseed oil in the same manner as is done in the preparation of blown oils (*see* above). This process is carried out in the manufacture of *linoleum*, when boiled linseed oil is allowed to run over 'scrim' (a light cotton fabric) hanging down from the ceiling of a high building, the temperature of which is kept at about 100° F. A portion of oil solidifies on the fabric; the oil which drains off is again pumped up and allowed to run down until the layers of the semi-solid mass have reached (after several weeks) the thickness of about half an inch. The solidified oil obtained by this method is termed 'scrim oil.'

Another method consists in passing a current of oxygen gas through linseed oil intermixed with a drier and heated by steam in jacketed pans. When the maximum amount of oxygen has been absorbed, the mass forms a thick viscous fluid, which will still flow while hot, but on cooling solidifies to a substance similar to the 'scrim oil.' During the 'blowing' partial hydrolysis and oxidation of the glycerol formed takes place, as notable quantities of acroleïn vapours escape. The semi-solid oil so obtained has not the same elastic properties which the 'scrim oil' possesses. (Both processes were invented by F. Walton, in 1860 and 1863 respectively.) The solid linseed oil is used in the manufacture of linoleum.

In a third process, known as the Taylor-Parnacott method, the linseed oil is thickened at a high temperature in a current of air.

For further details of the development of the linoleum industry, *see* J. Soc. Chem. Ind. 1919, 38, 26 T.

The *non-drying oils* are less readily attacked by oxygen, and solid fats only suffer a change if heated to a high temperature.

Action of ozone.—Ozone has no action on the glycerides of saturated fatty acids. The glycerides of unsaturated fatty acids are, however, easily acted on by ozone, each pair of doubly-linked carbon atoms absorbing 1 molecule of ozone.

According to Harries, 'perozonides' appear to be formed first, which are easily converted into stable ozonides (*see* OLEIC ACID)

Action of hydrogen.—Hydrogen gas under ordinary conditions or under pressure, or even if evolved in *statu nascendi*, either electrolytically or by means of sodium amalgam, has no action on the glycerides of higher unsaturated fatty acids, although it effects deodorisation of oils and fats.

Sabatier and Senderens, however, furnished by their method of reducing organic substances by means of hydrogen in the presence of finely divided metals, especially of finely divided nickel, an easy means of converting the glycerides of unsaturated fatty acids into practically completely saturated glycerides. Thus whale oil, cotton-seed oil, sesamé oil, &c., can be reduced to hard tallow-like substances which practically absorb no iodine. The same effect may be obtained by using colloidal palladium (Paal and Roth) or simply finely divided palladium. A somewhat considerable number of patents have been taken in this direction, all of them claiming modifications of the fundamental process of Sabatier and Senderens (*cf. Hydrogenated Oils*).

Action of chlorine.—Chlorine acts on oils and fats with evolution of hydrochloric acid, glycerides of chlorinated fatty acids being formed. At the same time chloro addition products are obtained. Hitherto it has not been possible to moderate the action of chlorine to such an extent that chloro addition products are obtained exclusively. Attempts are being made at present to find applications for chlorinated oils and fats in the arts.

Action of bromine.—Bromine acts in a manner similar to chlorine, although much less violently, so that it is possible to limit the reaction in the case of unsaturated glycerides so far, that bromo addition products only are obtained. Hence it is possible to obtain on a practical scale brominated oils and fats. Such products are recommended for pharmaceutical purposes. Thus bromine compounds of sesamé oil are sold as 'bromipin.'

Action of iodine.—Iodine is only slowly absorbed when mixed with oils or fats, but it does not yield substitution products. The assimilating power of oils or fats for iodine varies with the chemical constitution of their glycerides and also with the temperature, but never reaches that theoretical amount, which is indicated by the iodine value of oils and fats (*see* above). Iodised oils and fats have also been introduced into pharmacy. Thus 'iodipin' is a derivative of sesamé oil, containing about 25 p. c. of iodine.

Complete saturation of the unsaturated glycerides with halogens may be effected in the cold, if an alcoholic solution of iodine and mercuric chloride, or a solution of iodine monochloride or iodine monobromide in glacial acetic acid, is allowed to act on a dilute solution of oils or fats. The glycerides of the unsaturated acids absorb in that case 1 molecule of iodine chloride, or iodine monobromide, for each pair of doubly-linked carbon atoms, with the formation of saturated compounds. On this action is based one of the most important analytical operations practised in the examination of oils and fats, viz. the determination of the iodine value (*v. infra*).

Chloro-iodo, as also iodo-bromo fats and oils prepared by the above-described reaction are being introduced (or attempted to be introduced) into pharmacy.

Action of sulphur chloride.—Sulphur chloride acts energetically on fats. The reaction appears to consist in an absorption of the elements of sulphur chloride, much as iodine chloride is absorbed by the unsaturated carbon atoms (*see* above). The action of sulphur chloride would, therefore, appear to consist in the conversion of unsaturated (fatty acids or their) glycerides into saturated compounds.

In the two tables shown on page 660 a systematic examination made by Lewkowitsch (of the products obtained by the action of sulphur chloride) has been collated in a synoptic manner.

The sulphur chloride reaction finds technical application in the manufacture of rubber substitutes (*see Vulcanised Oils*, below).

Action of sulphur.—Sulphur has no chemical action on oils and fats in the cold. At higher temperatures, however, from 125° to 160°, all oils (since they contain glycerides of unsaturated fatty acids), notably linseed oil, castor oil, rape oil, cotton-seed oil, and marine animal oils, assimilate sulphur, and it would appear that the sulphur is absorbed much in the same manner as oxygen is absorbed by oils. On cooling, the sulphur does not separate out; on saponifying the sulphurised oils in the cold, sulphurised fatty acids are obtained, while very little sulphuretted hydrogen is evolved. On heating the sulphurised fatty acids to 130°-200°, however, sulphuretted hydrogen escapes in large quantities, and substitution of hydrogen in the molecule of the fatty substance by sulphur seems to take place. The action of sulphur on oils is made use of in the manufacture of vulcanised oils.

Vulcanised Oils.

Vulcanised oils, 'rubber substitutes,' are prepared by a process resembling the vulcanising of india-rubber, namely, either by treating oils with sulphur at a somewhat elevated temperature (comparable to the 'hot cure' of vulcanising india-rubber), or by treatment with sulphur chloride in the cold (corresponding to the 'cold cure' in the vulcanising of india-rubber). Hence the term 'vulcanised oils' is applied to these products.

Oils and Fats treated with Sulphur Chloride; 5 grams of Fat, 2 c.c. of Sulphur Chloride, and 2 c.c. of Carbon Disulphide.

A. *Products completely soluble in Carbon Disulphide.*

Class of oil	Kind of oil	—
Vegetable fats	Mowrah seed oil	Mass does not thicken
	Palm oil	
	Palm nut oil	
	Coconut oil	
Animal fats	Lard	
	Butter fat	
	Beef tallow	
	Mutton tallow	

B. *Products not completely soluble in Carbon Disulphide.*

Class of oil	Kind of oil	Solidifies after minutes		Soluble in carbon disulphide
		In the cold	On the water-bath	p.c.
Drying oils	Linseed	10	2	14·4
	Tung	1½	—	—
	Hemp seed	11	—	9·2
	Poppy seed	21	—	10·6
Fish oils	Japan fish	9	—	12·4
Liver oils	Cod liver, pure	15	—	4·4
	„ „ rancid	1½	—	6·4
Blubber oils	Seal	11	—	4·4
	Whale	13	—	3·0
Semi-drying oils	Cotton seed	20	4	24·0
	Sesamé	21	—	18·4
	Colza	23	—	2·8
	Rape	12	2	4·2
	Croton	18	—	25·4
Non-drying oils	Peach	26	—	4·8
	Almond, sweet	27	—	4·0
	Almond, bitter	28	—	3·4
	Arachis	30	—	6·0
	Olive	22	4	4·2
	Castor	½	at once	3·8
	Sheep's foot	36	—	6·0
	Horse's foot	20	—	13·6
	Neat's foot	23	—	9·4
	Lard	10	—	15·0
	Tallow	12	—	29·8

According to the process used, the vulcanised oils are differentiated in the trade as 'brown' (black) and 'white substitutes' respectively. The 'white substitutes' contain, therefore, a considerable proportion of chlorine, which is, of course, absent from the 'brown' (black) substitutes; thus it is possible easily to distinguish by chemical means between the two classes of rubber substitutes.

The white substitutes form a yellowish, elastic, crumbly substance of oily smell and neutral reaction; the brown (black) substitutes occur in commerce either as sticky lumps or as a coarsely ground powder.

To manufacture the white substitutes a suitable oil, especially rape oil, castor oil, soya-bean oil, maize (corn) oil (also sesamé or arachis oil), is dissolved in carbon tetrachloride, in a wooden, earthenware, or enamelled iron vessel. While the oil is agitated sulphur chloride is run in, the agitation being continued until the mass has solidified. The reaction is accompanied by evolution of hydrogen chloride.

The brown substitutes are manufactured by heating oils with sulphur at 160°. In the United States considerable quantities of brown substitutes are made from maize (corn) oil by heating 50 parts of oil at 240°, and mixing with it about 20 parts of melted sulphur.

Action of nitric acid.—Concentrated nitric acid attacks oils and fats, acting on them violently, with copious evolution of red fumes. Hot dilute nitric acid oxidises oils and fats gradually. *Fuming nitric acid*, in presence of concentrated sulphuric acid, reacts with linseed oil and castor oil to form 'nitrated' oils, the nature of which has not yet been fully investigated, although they have found technical application.

Nitrated Oils.

The nitrated oils are viscid liquids, heavier than water; thus the product obtained from linseed oil has the sp.gr. 1·112, that from castor oil 1·127. Nitrated castor oil is insoluble in carbon disulphide. The composition of these substances is not yet known; they contain 4–5 p.c. of nitrogen. Samples examined by the author had high saponification values, varying from 278·5 to 286·5. The most prominent property of these products is that of forming homogeneous compounds with nitro-cellulose. Thus a mixture of 1 part of nitrated castor oil with 9 parts of nitro-cellulose yields a product resembling ebonite. Solutions of these compounds in acetone have been proposed as varnishes, as a basis for paint, and for enamelling leather. By heating 'nitrated oils' at 130°, or by oxidising them with lead peroxide, rubber-like substances are obtained.

Action of nitrous acid.—On treatment with nitrous acid the non-drying oils become solid, or acquire the consistence of butter, according to the proportion of triolein (trierucin) they contain, triolein (trierucin) being converted into the solid isomeride trielaidin (tribrassidin). Drying and marine animal oils, on the other hand, remain liquid under the same treatment.

The different behaviour of the drying and marine animal oils is explained by the fact that while 'oleic' (erucic) acid is converted by nitrous acid into a solid isomeric, elaidic (brassidic) acid, linolic, linolenic, and clupanodonic acids remain liquid under the same conditions. Hence the non-drying oils yield solid masses, whereas the semi-drying and the drying and marine animal oils give more or less liquid products, according to the predominance of the glycerides of oleic acid. The fact that fuming nitric acid has the property of thickening olive and almond oils appears to have been observed first by Boyle in 1661. Poutet, in 1819, proposed this reaction, known as the *elaidin* test, for the detection of adulterants in olive oil. The test is carried out in the following manner (viz. in the modification suggested by Archbutt): 18 grams of mercury are placed in a dry stoppered 50-c.c. cylinder, and 15·6 c.c. of nitric acid, sp.gr. 1·42, are added from a burette. The nitrous acid is entirely absorbed with production of a green coloration; as long as the reagent retains its green colour, it is fit for use. Eight grams of the reagent are shaken up with 96 grams of the oil in a wide-mouthed stoppered bottle, placed in water at the required temperature, and again shaken at intervals of 10 minutes during 2 hours.

In the early history of oil analysis, before the present scientific (quantitative) methods (*v. infra*) were known, this test afforded some guidance. It was even attempted to base a classification of the oils on it, but such a classification must lead to inconclusive results. Although this test was somewhat extensively practised here as also in France, it may be said to have been abandoned in *this* country, as the results indicated by the elaidin test are in every respect much less valuable than those furnished by the iodine test. In the comparative examination of almond oil and its congeners this test may afford some little information of a discriminative nature. In order to obtain trustworthy results, it is indispensable to institute side by side with the oil under examination, under exactly the same conditions, tests with standard oils of known purity.

Action of concentrated sulphuric acid.—If oils, which, of course, contain glycerides of unsaturated fatty acids, be mixed with the acid very gradually, and at a low temperature, glycerides of a complex constitution are formed. The formation of these products is indicated by a notable rise of temperature. (The antiquated 'Maumené test' is based on the measurement of the rise of temperature.) Thus, on treating olive oil with concentrated sulphuric acid a compound is obtained which may be regarded (Geitel) as a mixed glyceride of oleic acid, stearic acid, hydrogen sulphate, and hydroxystearic acid, having the formula—

$$C_3H_5[O{\cdot}C_{18}H_{33}O][O{\cdot}C_{18}H_{34}(SO_4H)O][O{\cdot}C_{18}H_{34}(OH)O]$$

This product is very unstable in the presence of water. On boiling with water it is rapidly decomposed into compounds which form a complete emulsion with water and fats; on agitating the emulsion with steam, complete hydrolysis to glycerol and fatty acids is brought about (*see* SAPONIFICATION). This reaction is employed on a large scale in the manufacture of Turkey-red oils.

Turkey-red Oil.

Turkey-red oil is a fatty substance used in the preparation of the cotton fibre for dyeing and printing Turkey-red. The part which the Turkey-red oil plays is not fully understood; opinions differ as to whether it exercises a physical or a chemical action. The advocates of the former explanation assume that the oil protects the lake formed on the fibre, much as boiled linseed oil serves to protect a painted surface. The supporters of the chemical theory hold that the Turkey-red oil combines with alumina and finally with the colouring matter to form a compound lake. In those cases, however, where chemical combination with formation of a lake is excluded on account of the chemical constitution of the colouring matter, the physical theory appears to commend itself. Hence Turkey-red oil is not a mordant proper, but acts as a fixing agent in so far as it imparts to the dyed fabric a better and superior lustre, which does not belong to the unoiled fibre. The sulphonated oils would appear to the author to be absorbed by the fibre in the same manner as glycerol (from soft soaps) is fixed on the fibre on washing woollen goods.

Before the process of sulphonating castor oil was discovered (1875), rancid olive oil and sulphonated oils (such as sulphonated olive oil) were used as Turkey-red oils. At present Turkey-red oil is prepared by allowing concentrated sulphuric acid to run slowly into castor oil, with constant stirring, taking care that the temperature of 35° is not exceeded. If necessary, the mass must be cooled, for secondary reactions take place at temperatures above 35° with liberation of sulphurous acid. The product is then mixed with a small quantity of water and the dilute acid allowed to settle out as a lower layer. This is drawn off and the oil washed with a solution of Glauber's salt, until the washings are only slightly acid. Finally ammonia is added, until a sample gives a clear solution with a small quantity of water. Some manufacturers use soda instead of ammonia, or a mixture of ammonia and soda. Since the sulphonated oil is not completely neutralised by alkali, the resultant product still possesses a strong acid reaction.

The portion of sulphonated castor oil soluble in water contains principally ricinoleo-sulphuric acid, which is easily hydrolysed to some extent by boiling with dilute acids into sulphuric acid and ricinoleic acid, whereas another portion is converted into inner anhydrides of ricinoleic acid. The portion of castor Turkey-red oil insoluble in water consists chiefly of free ricinoleic acid and small quantities of neutral (unacted-on) oil, and also of anhydrides of ricinoleic acid (*cf.* also Lewkowitsch, Chem. Tech. [iii.] 155 *et seq.*).

For a summary of the principal methods of analysing Turkey-red oil, *see* J. Soc. Chem. Ind. 1912, 31, 105. The standard adopted by the American Leather Chemists Assoc. is based on a total fatty oil content of 70 p.c.

At a temperature exceeding 100° *concentrated sulphuric acid* reacts energetically with all oils and fats, partly carbonising them and hydrolysing them, whereby glycerol and sulpho compounds of fatty acids are formed. On steaming, the latter are decomposed into sulphuric acid and fatty acids. On this reaction is based the 'acid saponification' process employed in the candle industry (*see* SAPONIFICATION).

Dilute sulphuric acid, even at temperatures of 100°, does not act on oils and fats (Lewkowitsch).

A dilute solution of sulpho-aromatic compounds (Twitchell's reagent) readily effects hydrolysis of the glycerides (*see* SAPONIFICATION).

Action of hydrochloric acid.—Hydrochloric acid exercises a very slow action at the ordinary temperature; at higher temperatures it behaves as a catalytic agent, and accelerates considerably the hydrolysis of oils and fats. Obviously, hydrochloric acid does not take part in the chemical change, but merely accelerates the hydrolysis primarily brought about by water (Lewkowitsch, J. Soc. Chem. Ind. 1903, 67). If a thorough intermixture as in an emulsion could be effected between fat and water, hydrolysis would proceed much more rapidly than was observed in Lewkowitsch's experiments, for it has been shown by him experimentally that the catalytic action of hydrochloric acid takes place even at the ordinary temperature in course of time.

Action of caustic alkalis and alkaline earths.—Caustic alkalis and alkaline earths, if treated with oils and fats in the presence of water, act in the first instance as catalysts bringing about rapid hydrolysis of the oils and fats. The free fatty acids formed combine with the caustic alkalis and alkaline earths, yielding as a secondary product soaps of the alkaline metals and the alkaline earths. On this reaction are based the great industries of soap- and candle-making (*see* SAPONIFICATION and SOAP).

Action of ammonia and aromatic bases.—Ammonia hydrolyses oils and fats to some extent if acting under pressure (*see* SAPONIFICATION). Alcoholic ammonia, on prolonged standing in the cold with oils and fats, yields amides.

Aromatic bases, such as aniline, &c., on being heated under pressure at 210°, react similarly with oils and fats. In the case of aniline, the reaction was stated to take place according to the following equation—

$$C_3H_5(OR)_3+3C_6H_5.NH_2=C_3H_5(OH)_3+3C_6H_5\,NHR$$

But it has been shown that this reaction is unworkable on a practical scale.

In the case of hydroxylamine, hydroxamic derivatives of fatty acids are obtained, together with glycerol, as is exemplified by the following equation—

$$C_3H_5(OR)_3+3NH_2OH=C_3H_5(OH)_3+3R(NOH)OH$$

SYSTEMATIC EXAMINATION OF OILS AND FATS.

The most frequent problem in the examination of oils and fats is to identify a given oil or fat. As the natural oils and fats represent a complicated mixture of not only simple triglycerides, but also of mixed triglycerides, it is impossible, in the present state of our knowledge, to indicate a definite course of analysis, applicable to all circumstances, such as is the case in inorganic quantitative and qualitative analysis. Yet, by adopting a systematic plan of examination, it is possible, in the majority of cases, to identify a given sample of one individual oil or fat and to ascertain whether it is a pure or adulterated specimen. In the latter case, the nature of the adulterant can generally be ascertained. The methods described below may also be used to identify a mixture of two or more oils and fats and to ascertain the presence and recognise the nature of the constituents of the mixture, at least qualitatively. Frequently, it is even possible to determine quantitatively the proportion in which the component parts have been mixed. The greater the number of component oils and fats in a mixture, the more difficult becomes the examination, but if the analyst proceeds logically and combines the methods described below in a suitable manner, it will be possible in many cases to ascertain the composition of a complicated mixture with such accuracy as suffices for technical purposes.

If it be borne in mind that adulteration has almost become a fine art, and that it is being practised with the full armour of scientific knowledge by experts who are frequently some years ahead of the knowledge possessed by the analytical chemist, it will readily be understood that the analyst must select special methods and tests and adapt them to each case.

A systematic examination will deal, in the first instance, with the natural oils and fats themselves. The methods applied to this purpose may be broadly divided into physical and chemical methods.

Since all natural oils and fats contain as a common constituent the radical glycerol, or in other words, since all oils and fats yield glycerol on saponification, the difference of the several glycerides can only be conditioned by, or due to, the difference of the fatty acids contained in the glycerides. Hence it follows that in the second place the examination of the fatty acids themselves will prove of great importance. A section is, therefore, devoted specially to the *examination of the fatty acids.*

The identification of an oil or fat as a *vegetable* or *animal* oil or fat rests, as explained above, on the occurrence of phytosterol or cholesterol in vegetable or animal oils respectively. Hence the examination of the 'unsaponifiable' furnishes an excellent means of differentiating between vegetable and animal oils. From this point of view alone, the examination of the unsaponifiable matter becomes a valuable aid in the systematic course of examination. Obviously, if a mixture of vegetable and animal oils be given, a mixture of phytosterol and cholesterol will be obtained, the resolution of which into its components may be required in many cases. The examination of the 'unsaponifiable' becomes, furthermore, most important in those cases in which unsaponifiable oils have been used as adulterants.

One of the most important problems required to be solved by analysis is to ascertain whether a sample is pure or adulterated with hydrocarbons. Thus the examination of the unsaponifiable matter, provided it exceed 1 or at most 2 p.c. of an oil or fat, furnishes an important clue as to adulteration. It will, therefore, be most convenient to subdivide this section under the following three heads:—

I. Examination of Oils and Fats.
II. Examination of Fatty Acids.
III. Examination of the Unsaponifiable Matter.

Correct interpretation of indications afforded by the following tests and strict logical reasoning enable us, in the majority of cases, to narrow down, by a process of elimination, the range of possible constituents of a mixture to such an extent that the practised analyst will but rarely be confronted with the impossibility of arriving at approximate accuracy at least. In order to facilitate the interpretation of the results obtained with the aid of the following methods, the characteristic values of the most important oils and fats are arranged in a practically natural system in the tables collated at the end of this article. With the aid of these tables, it will not be difficult to identify a single individual. If, in the course of a commercial analysis, the limits of our present knowledge have been reached, the application of methods that have not yet been used for the case under consideration will suggest itself. This happens not infrequently in the examination of technical products.

For a number of examples, giving a clue as to how complicated mixtures may be examined, the reader is referred to Lewkowitsch's Chem. Techn.

I. Examination of Oils and Fats.

The methods described under this head may be broadly divided into physical and chemical methods. With the physical methods may be incorporated suitably the so-called organoleptic methods, comprising odour, taste, colour, and consistence.

Examination by Physical Methods.

Odour and *taste* are especially characteristic of the oils of marine animals. In the case of solid fats, a *red colour* suggests raw palm oil. The *consistence* at ordinary temperature gives a rapid indication as to whether the specimen belongs to oils or fats. In most cases, however, these organoleptic methods afford some help to the expert only. In the case of edible oils and fats, odour and taste must be considered as very important criteria, as rancidity is most readily recognised by taste. The following physical methods are of importance:—

Specific gravity.—The specific gravity of the liquid oils is best determined by means of a pyknometer or a hydrostatic balance. In the case of solid fats, the specific gravity is most readily taken at a temperature at which the fat is liquid. Suitable temperatures are 40° in the case of fats liquid at that temperature. In other cases, the determination is made at temperature of boiling water. In the tables given at the end of this article, the specific gravities have been added. Speaking generally, it may be stated that the specific gravity number does not afford such important information as was believed to be the case at a time before the quantitative methods had been worked out. Still, castor oil would be recognised at once by its exceptionally high specific gravity.

Melting and solidifying points.—Fats do not melt so sharply as is the case with chemically pure substances. Hence fats, if examined in a capillary tube, melt within several degrees, the fats softening at first, then melting at the edge of the substance, becoming transparent at the same time until they are melted completely. Therefore, some uncertainty obtains as to which temperature should be regarded as the melting-point. Some observers denote as melting-point that temperature at which the fat which has been allowed to solidify in a small tube open at both ends softens sufficiently to be driven up by the hydrostatic pressure of water. Others, again, denote that temperature as the melting-point at which the fat drops off the mercury bulb of a thermometer, which has previously been dipped into the melted fat and allowed to cool. Hence, it is imperatively necessary to state in each case by what method the melting-point has been determined. It is, therefore, customary in commerce to agree between buyer and seller as to the method. It is important to note that the freshly melted sample does not indicate the true melting-point, which is only ascertainable after the sample has been kept for 24 hours. In the case of cacao butter, even an interval of two or more days is required. The melting-points of most fats are given in the tables at the end of this article. It may be pointed out that, as a rule, it is preferable to determine the solidifying-point of the *fatty acids* prepared from the oils and fats (*v. infra*).

Refractive index.—The determination of the refractive index—which can be carried out in a very simple and rapid manner, thanks to the construction of the oleorefractometer by Amagat and Jean, and especially that of the butyro-refractometer by Zeiss—forms one of the simplest preliminary tests in the examination of oils and fats, and especially in the examination of butter fat and lard. Owing to the ease and rapidity with which this 'characteristic' can be determined, the objections previously raised against observations with the aid of an ordinary refractometer have given place to a widely held over-estimation of the importance of this test. The observer should, therefore, be warned against placing too much reliance on the indications of the refractometer and, as stated already, should only consider it as a preliminary test, the indications of which must be supported and corroborated by other methods (*cf.* Lewkowitsch, Chem. Techn.).

Thus, in the case of butter fat, a glance at a sample in the refractometer may decide whether the specimen is grossly adulterated or not. But if the number be only slightly abnormal, or even if so-called 'normal numbers' have been found, the purity of the specimen is not yet proved, as it is easy, *e.g.*, to prepare specimens of margarine containing coconut oil which show the same refraction as a normal butter fat. Even if abnormal numbers have been obtained, this would not prove adulteration. It would be entirely erroneous to look upon the refractometric method as permitting the identification of an oil or fat. Equally erroneous would be the attempt to deduce quantitative interpretations as to the proportions of an adulterant from the deviation from normal numbers. The refractive indices of most oils are contained in the tables at the end of this article. By comparing these numbers with the iodine values, it will be gathered that there is a certain, although by no means definite, correlation between the refractive indices and the iodine values. For the description of refractometers, see Lewkowitsch, Chem. Techn., and art. REFRACTOMETER.

Rotatory power.—The determination of the rotatory power has not been practised extensively in the examination of oils and fats for the reasons stated above. Since, however, oils belonging to the 'Chaulmoogra group' can be identified readily—and indeed have been the means of identifying the 'Cardamom oil'—(see CHAULMOOGRA OIL GROUP) the polarimetric method is destined to find a wider application.

Solubility test.—Almost all oils and fats are easily soluble in the usual organic solvents; hence the solubility test has little importance. Only castor oil is distinguished from all other natural oils and fats by its ready solubility in alcohol (*see* CASTOR OIL).

Examination by Chemical Methods.

The most important chemical methods employed in the examination of oils and fats have for their object the determination of certain numerical values which depend on the nature of the fatty acids occurring in the oils and fats. These numbers represent only a measure of the amounts of the several fatty acids or fatty acid groups present in the oils and fats, without, however, expressing their absolute quantity. Hence these methods have been suitably termed 'quantitative reactions.' In addition to these quantitative reactions there are also at the disposal of the analyst a number of 'qualitative reactions.'

(*a*) *Quantitative Methods.*

The numerical values which are ascertained by means of quantitative methods are divided by the author into two classes.

(*a*) 'Characteristics,' *i.e.* those numbers which depend entirely on the specific nature of an oil or fat and hence assist most materially in identifying a given oil or fat.

(*b*) 'Variables,' *i.e.* those numbers which allow us to judge of the quality of a given oil or fat. These numbers naturally vary with the state of purity, rancidity, age, etc., of a given specimen.

The *characteristics* will be considered under the following heads:

(1) Saponification Value.
(2) Iodine Value.
(3) Reichert (Reichert-Meissl or Reichert-Wollny) Value.

The *variables* will comprise:

(1) Acid Value.
(2) Amount of Glycerol, expressed in per cent.
(3) Amount of Unsaponifiable Matter, expressed in per cent.

Midway between these two classes stands the 'acetyl value' which, in some cases, must be considered a 'characteristic,' whereas in other cases it is a 'variable.'

(A) Characteristics.

1. *Saponification Value.*

The saponification value indicates the number of milligrams of potassium hydroxide required for the complete saponification of one gram of an oil or fat; in other words, it represents the amount of potassium hydroxide, expressed in tenths per cent., required to neutralise the total fatty acids in one gram of an oil or fat.

The saponification value is determined as follows:—Weigh off accurately, in a flask holding 150–200 c.c., 1·5 to 2 grams of the purified and filtered sample. Next run into the flask 25 c.c. of an approximately semi-normal alcoholic solution of potassium hydroxide measuring it off by means of a pipette. It is not necessary to add exactly 25 c.c., but care must be taken that for each determination precisely the same volume is used. Then attach a long cooling tube or an inverted condenser to the flask, and heat on the boiling water-bath for half an hour so that the alcohol is kept simmering; in order to accelerate saponification, the contents should be mixed by imparting to the flask a rotatory motion. When the saponification is deemed to be complete, allow the solution to cool a little, add 1 c.c. of a 1 p.c. phenolphthalein solution and titrate back the excess of potassium hydroxide with semi-normal hydrochloric acid. In case too much alcohol has been volatilised, it is advisable to add some alcohol (previously neutralised) or to add normal acid at first and to complete the titration with semi-normal acid.

It is necessary to make a blank test by treating the same amount of alcoholic potassium hydroxide in exactly the same manner as is done with the sample.

Example.—Weighed off 1·532 grams of olive oil, and saponified with 25 c.c. of alcoholic potassium hydroxide solution. Required for titrating back 12·0 c.c. semi-normal acid; further, required for the blank test, 22·5 c.c. of the same acid. Therefore a quantity of potassium hydroxide, corresponding to $\frac{(22\cdot5-12\cdot0)0\cdot0561}{2}$ grams $=294\cdot5$ milligrams KOH was employed for saponification. Hence, used for 1 gram of fat $\frac{294\cdot5}{1\cdot532}$ milligrams KOH$=192\cdot2$ milligrams KOH. The saponification value of the sample of olive oil is, therefore, 192·2.

The saponification values of neutral glycerides (esters of fatty acids) vary, of course, with the nature of the fatty acids; the lower the molecular weight of the fatty acids (or, what amounts to the same, of the esters), the more potassium hydroxide will be required to neutralise the fatty acids of 1 gram of oil or fat, or, in other words, the higher will be the saponification value. To illustrate this more clearly, the saponification values of some pure triglycerides are subjoined in the table on next page.

It will be gathered from the numbers given in the tables at the end of this article that the saponification values of the majority of natural oils and fats lie in the neighbourhood of 193 to 195. In the case of unknown samples, wide deviations from this number in either direction will at once enable the analyst to single out individual oils or fats. Thus, oils belonging to the rape oil group are characterised by a considerably lower saponification value, viz. about 175. The lower saponification values of these oils find their explanation in the large proportion of erucin they contain. In the case of castor oil, the lower value is due to the presence of hydroxylated fatty acids.

On the other hand, large deviations in the opposite direction enable us to single out a

Saponification Values of Triglycerides.

Triglycerides	Formula	Molecular weight	Saponification value
Simple Triglycerides—			
Acetin	$C_3H_5(O{\cdot}C_2H_3O)_3$	218	772·0
Butyrin	$C_3H_5(O{\cdot}C_4H_7O)_3$	302	557·3
Valerin	$C_3H_5(O{\cdot}C_5H_9O)_3$	344	489·2
Caproin	$C_3H_5(O{\cdot}C_6H_{11}O)_3$	386	436·1
Caprylin	$C_3H_5(O{\cdot}C_8H_{15}O)_3$	470	358·1
Caprin	$C_3H_5(O{\cdot}C_{10}H_{19})O_3$	554	303·7
Laurin	$C_3H_5(O{\cdot}C_{12}H_{23})O_3$	638	263·8
Myristin	$C_3H_5(O{\cdot}C_{14}H_{27}O)_3$	722	233·1
Palmitin	$C_3H_5(O{\cdot}C_{16}H_{31}O)_3$	806	208·8
Stearin	$C_3H_5(O{\cdot}C_{18}H_{35}O)_3$	890	189·1
Olein	$C_3H_5(O{\cdot}C_{18}H_{33}O)_3$	884	190·4
Linolin	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	191·7
Hydnocarpin	$C_3H_5(O{\cdot}C_{16}H_{27}O)_3$	794	211·9
Chaulmoogrin	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	191·7
Linolenin	$C_3H_5(O{\cdot}C_{18}H_{29})O_3$	872	193·0
Clupanodonin	$C_3H_5(O{\cdot}C_{18}H_{27}O)_3$	866	194·3
Ricinolein	$C_3H_5(O{\cdot}C_{18}H_{33}O_2)_3$	932	180·6
Arachin	$C_3H_5(O{\cdot}C_{20}H_{39}O)_3$	974	172·7
Erucin	$C_3H_5(O{\cdot}C_{22}H_{41}O)_3$	1052	160·0
Cerotin	$C_3H_5(O{\cdot}C_{26}H_{51}O)_3$	1226	137·3
Melissin	$C_3H_5(O{\cdot}C_{30}H_{59}O)_3$	1394	120·7
Mixed Triglycerides—			
Oleodipalmitin (Dipalmito-olein)	$C_3H_5(O{\cdot}C_{16}H_{31}O)_2(O{\cdot}C_{18}H_{33}O)$	832	202·3
Stearodipalmitin (Dipalmitostearin)	$C_3H_5(O{\cdot}C_{16}H_{31}O)_2(O{\cdot}C_{18}H_{35}O)$	834	201·8
Oleopalmitostearin (Stearopalmito-olein)	$C_3H_5(O{\cdot}C_{16}H_{31}O)(O{\cdot}C_{18}H_{33}O)(O{\cdot}C_{18}H_{35}O)$	860	195·7
Palmitodistearin (Distearopalmitin)	$C_3H_5(O{\cdot}C_{18}H_{35}O)_2(O{\cdot}C_{16}H_{31}O)$	862	195·2
Oleodistearin	$C_3H_5(O{\cdot}C_{18}H_{33}O)(O{\cdot}C_{18}H_{35}O)_2$	888	189·5
Dioleostearin	$C_3H_5(O{\cdot}C_{18}H_{33}O)_2(O{\cdot}C_{18}H_{35}O)$	886	189·9

number of oils and fats, and hence render their recognition a comparatively easy task. Thus the high saponification value of the fluid portion of dolphin and porpoise oils are indicative of a high proportion of lower fatty acids. A prominent example of a fat having a characteristically high saponification value is butter fat; hence by the saponification value alone, butter fat can be differentiated from margarine. High saponification values are also characteristic of fats consisting preponderantly of glycerides of myristic acid, and especially of the members of the coconut oil and dika fat groups.

If mineral oils or other unsaponifiable substances are intermixed with the fatty substances, it is obvious that the indications furnished by the saponification values alone would, if accepted without any further investigation, be entirely misleading, since the unsaponifiable matter depresses the saponification value. Thus, to take an example, an oil having the saponification value 193, if adulterated with 10 p.c. of mineral oil, would show a saponification value of about 175, and might, therefore, be mistaken for a rape oil if no further tests were applied.

If colophony (rosin) be dissolved in the fatty substance, the saponification value will remain unaffected, provided rosin of about the same saponification value be used. With a rosin of a lower saponification value than that of the oil or fat, the saponification value of the mixture would, of course, be somewhat depressed.

2. *Iodine Value.*

The iodine value indicates the percentage of iodine chloride absorbed by an oil or fat, expressed in terms of iodine. Theoretically, the acids belonging to the oleic and ricinoleic series should absorb two atoms of chlorine or iodine, or one molecule of iodochloride. Hence the glycerides of these acids should absorb six atoms of chlorine or iodine, or three molecules of iodochloride. Similarly, the acids of the linolic series should assimilate four atoms of halogens or two molecules of iodochloride; whereas the members of the chaulmoogric series would assimilate only two atoms of halogens or one molecule of iodochloride, on account of the cyclic arrangement of some carbon atoms; the members of the linolenic series six atoms of halogens or three molecules of iodochloride, and the members of the clupanodonic series eight atoms of halogens or four molecules of iodochloride.

These rules apply, however, only to doubly-linked carbon atoms. Trebly-linked pairs of carbon atoms, the occurrence of which in fatty acids (and hence in natural oils and fats) has not yet been definitely ascertained, do not absorb the theoretical amount of halogens.

The determination of the iodine value was introduced into fat analysis by von Hübl and is carried out either in the manner indicated originally by Hübl or in the modification proposed by Wijs. The author's experience leads him to recommend the latter modification as more convenient and trustworthy. Since, however, Wijs' method has not yet been universally adopted, both methods will be described here.

Hübl's method.—From 0·15 to 0·18 gram of a drying or a marine animal oil, 0·2–0·3 gram of a semi-drying oil, 0·3–0·4 gram of a non-drying oil, or 0·8–1·0 gram of a solid fat, is weighed off accurately, and placed in a bottle of 500–800 c.c. capacity provided with a well-ground stopper. The weighing off is best done in a small weighing bottle, the cork of which is fitted with a finely drawn out tube so that a certain number of drops of an oil or of a previously melted fat can be easily taken out with the aid of an india-rubber tube fixed on the top. The fat is dissolved in 10 c.c. of chloroform, or carbon tetrachloride, and 25 c.c. of an 'iodine solution' are run in from a pipette (This iodine solution is prepared by dissolving 25 grams of pure iodine on the one hand, and 30 grams of mercuric chloride on the other hand, in 500 c.c. of 95 p.c. of alcohol. Both solutions are kept separate and the quantity required for an estimation must have been prepared 24 hours before by mixing equal volumes of the two solutions. The mixture must not be used immediately after preparation, since the solution of iodochloride rapidly changes its titre after preparation. Although even after 24 hours' standing, the mixture still slowly changes its titre, it remains sufficiently constant during an estimation.) The pipette is always emptied in the same manner: this is best done by allowing it to drain until two or three drops have run out. In order to prevent loss of iodine by volatilisation, it is advisable to moisten the stopper with potassium iodide solution. The solvent and the iodine solution should give a clear solution on shaking, otherwise more solvent must be added The bottle is then allowed to stand in a dark place. Should the deep brown colour of the solution disappear after a short time, another 25 c.c. of the iodine solution must be run in, an excess of iodine being essential for the reaction to become complete. The solution, after two hours, must still exhibit a deep brown colour. Most of the iodine is absorbed during the first two hours. The reaction then slows down; it cannot be considered complete in less than six to eight hours in the case of solid fats and non-drying oils, and twelve to eighteen hours in the case of drying oils and fish oils. Semi-drying oils require 8 to 10 hours. After standing for the requisite number of hours, from 15 to 20 c.c. of a 10 p.c. potassium iodide solution are run in. the liquid is well shaken and then diluted with 400 c.c. of water. The appearance of a red precipitate of mercuric iodide at this stage would indicate that an insufficient amount of potassium iodide had been employed, therefore more must be added. The excess of free iodine, part of which will be in the aqueous solution, whereas the remainder is dissolved in the solvent, is titrated with a standardised thiosulphate solution by running the latter into the bottle until, after repeated agitation, both the aqueous and the chloroform (carbon tetrachloride) layers are but faintly coloured. A few drops of a starch solution are next added and the titration is then brought to an end. Immediately before or after this titration, 25 c.c. of the original iodine solution are standardised in exactly the same manner. The difference between the two results corresponds to absorbed halogen, and is calculated in terms of iodine to units per cent. of the sample. The number thus found is termed the iodine value.

Example.—Weighed off 0·3394 gram of lard, dissolved in 10 c.c. of carbon tetrachloride, added 25 c.c. of iodine solution, which required in a blank experiment 60·9 c.c. of thiosulphate solution, 16·45 c.c. of which were equivalent to 0·2 gram of iodine. For titrating back the excess of iodine in the estimation, there were required 39·6 c.c. of thiosulphate solution Hence, the absorbed iodine corresponds to 60·9–39·6 = 21·3 c.c. of thiosulphate solution.

Since 16·45 c.c. of thiosulphate solution are equivalent to 0·2 gram of iodine, 21·3 c.c. correspond to $\frac{0\cdot2\times21\cdot3}{16\cdot45}=0\cdot2589$ gram of iodine. Hence 0·3394 gram of lard absorbs 0·2589 gram of iodine, or 100 grams absorb $\frac{0\cdot2589\times100}{0\cdot3394}$ $=76\cdot28$ grams of iodine. The iodine value of the lard is, therefore, 76·28.

(With regard to the theory of the complicated chemical reactions occurring in Hübl's solution, *v.* Lewkowitsch, Chem. Techn.)

Wijs' method.—The solution required for Wijs' method is prepared by dissolving separately 7·9 grams (the theoretical figure is 7·9617) of iodine trichloride and 8·7 grams (the theoretical figure is 8·6670) of iodine in glacial acetic acid on the water-bath, taking care that the solutions do not absorb moisture. The two solutions are then poured into a 1000 c.c. flask, and the flask is filled up to the mark with glacial acetic acid.

A cheaper way of preparing the solution is to dissolve 13 grams of iodine in a litre of glacial acetic acid, then to determine accurately its content of iodine, and to pass washed and dried chlorine gas through the solution until the titre of the original iodine solution is doubled. A little experience will readily show when this point is reached, as a very distinct change of colour takes place when all the iodine has been converted into iodine monochloride.

The glacial acetic acid must be pure, and should be tested by heating with potassium dichromate and concentrated sulphuric acid; even after prolonged standing a green tinge should not be noticeable.

The iodine value is determined in exactly the same manner as described above for the Hubl solution. It is, however, preferable to use carbon tetrachloride, since chloroform frequently contains alcohol. Wijs' iodine solution can be used immediately after preparation and possesses the great advantage over Hübl's solution in that it keeps its strength unchanged for a considerable length of time. Hence, in ordinary work, a blank test is not required in each case, and the determination of the iodine value can be carried out almost as rapidly as the determination of the saponification value. Wijs' solution has the further advantage that in the case of fats and non-drying oils the absorption of iodochloride is complete after half an hour, in the case of semi-drying oils after about 1 hour, and in the case of drying oils and marine animal oils in from 2 to 6 hours, according to the unsaturation of the glycerides.

The iodine value is one of the most important characteristics in the analysis of oils and fats, as this number permits us to classify the oils and fats in a practically natural system. This will be gathered from an inspection of the tables given at the end of this article.

If a given sample of oil or fat contains the glycerides of one unsaturated fatty acid of known composition in admixture with glycerides of saturated fatty acids, it is possible to calculate the absolute amount of the glyceride of that unsaturated fatty acid. In cases of this kind, the following table will be found useful. It will also guide the analyst as to the direction which further research should take in the case of samples of unknown composition, when, of course, the proportion of glycerides of unsaturated fatty acids cannot be calculated from the iodine value alone.

IODINE VALUES OF UNSATURATED FATTY ACIDS AND OF THEIR TRIGLYCERIDES (Lewkowitsch).

Acid	Formula	Iodine value of	
		Fatty acid	Triglyceride
Tiglic .	$C_5H_8O_2$	254·00	225·44
	$C_{12}H_{22}O_2$	128·28	120·57
	$C_{14}H_{26}O_2$	112·39	106·42
Hypogaeic . Physetoleic .	$C_{16}H_{30}O_2$	100·00	95·25
Hydnocarpic .	$C_{16}H_{28}O_2$	100·79	95·97
Oleic . . Rapic . .	$C_{18}H_{34}O_2$	90·07	86·20
Erucic . .	$C_{22}H_{42}O_2$	75·15	72·43
Linolic. . Tariric. .	$C_{18}H_{32}O_2$	181·42	173·58
Chaulmoogric .	$C_{18}H_{32}O_2$	90·71	86·79
Linolenic . isoLinolenic .	$C_{18}H_{30}O_2$	274·10	262·15
Clupanodonic .	$C_{18}H_{28}O_2$	368·11	351·96
Ricinoleic . .	$C_{18}H_{34}O_3$	85·23	81·76
Mixed Triglycerides—			
Myristopalmito-olein . .	—	—	31·59
Oleodipalmitin .	—	—	30·53
Oleopalmitostearin .	—	—	29·73
Oleodistearin .	—	—	28·60
Dioleostearin .	—	—	58·09

3. *Reichert* (*Reichert-Meissl, Reichert-Wollny*) *Value.*

The Reichert (or Reichert-Meissl) value indicates the number of cubic centimetres of decinormal potash or soda solution requisite for the neutralisation of that portion of the soluble volatile fatty acids which is obtained from 2·5 (or 5) grams of an oil or fat by the Reichert distillation process.

Reichert, who originated this method, used 2·5 grams of fat. Meissl, as also Wollny, proposed 5 grams, which is now generally employed. It must, however, be pointed out that the Reichert-Wollny value is not twice the Reichert value, but usually 2·2 times the Reichert value. Since Wollny's process has been adopted by a Joint Committee of the Government Laboratory and the Society of Public Analysts as the standard method for the determination of the soluble volatile fatty acids in margarine and butter the Reichert-Wollny process alone will be described.

Reichert-Wollny process.—Five grams of liquefied fat are introduced into a 300 c.c. flask of the form shown in Fig. 3 (length of neck 7–8 cms., width of neck 2 cms.). Two c.c. of a sodium hydroxide solution, prepared by dissolving 98 p.c. sodium hydroxide in an equal weight of water—protected from the action of atmospheric carbon acid—and 10 c.c. of (about 99 p.c.) alcohol are added, and the mixture is heated for 15 minutes under a reflux condenser, connected with the flask by a T-piece, in a bath containing boiling water. The alcohol is evaporated off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water, which has been kept boiling for at least 10 minutes (to drive out all dissolved carbonic acid, the retention of which would vitiate the result), are added, and the flask is heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube, 7 mm. wide, and 15 cms. from the top of the cork to the bend. At a distance of 5 cms. above the cork is a bulb 5 cms. in diameter. The flask is supported on a circular piece of asbestos, 12 cms. in diameter, having a hole in the centre 5 cms. in diameter, and is first heated by a very small flame, to melt the insoluble fatty acids, but the heat must not be so great as to cause the liquid to boil; when fusion is complete the heat is increased, 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (from 28 to 32 minutes); the distillate is shaken, 100 c.c. are filtered off, transferred to a beaker, 0·5 c.c. of phenolphthalein solution (1 gram in 100 c.c. alcohol) is added, and the filtrate is titrated with decinormal soda or baryta solution. In precisely the same manner (with the same reagents), a blank test should be made, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained in the blank experiment, is multiplied

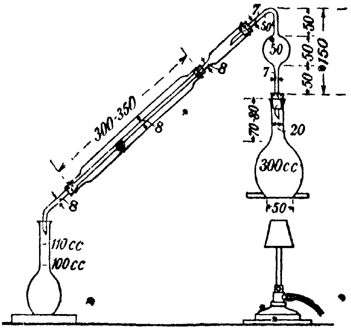


FIG. 3.

by 1·1. The number so found is the Reichert-Wollny value.

The Reichert-Meissl value (see tables at the end of this article) is practically identical with the Reichert-Wollny value. The Reichert-Meissl value of the majority of oils and fats, that is of those the saponification value of which is less than 200, is below 0·5. All oils and fats the saponification value of which exceeds 200 are characterised by Reichert-Woollny values exceeding 1·0. The Reichert-Meissl value furnishes important indications regarding the nature of an oil or fat; thus butter fat is most prominently characterised by its high Reichert-Meissl value of about 27 to 29; the fats belonging to the coconut oil group by Reichert-Wollny values of 5 to 8, and dolphin and porpoise oils by Reichert-Meissl values varying from 47 to 120 (see tables at the end of this article).

Leffmann and Beam proposed the method of saponification with a concentrated solution of sodium hydroxide in glycerol. This process is convenient owing to its rapidity, and has therefore been introduced by Polenske in the examination of butter fats, suspected of being adulterated with coconut oil. The method is carried out as follows: 5 grams of butter fat are placed in a 300 c.c. flask and heated with 20 c.c. of a solution of sodium hydroxide in glycerol (prepared by dissolving 100 grams of sodium hydroxide in an equal weight of water and mixing 20 c.c. of this solution with 180 c.c. of pure concentrated glycerol) over a naked flame for 2–3 minutes, until the water has evaporated off and the liquid has become clear. The values obtained by Leffmann and Beam's method are practically identical with those furnished by the Reichert-Wollny process, as the author can testify from his own experience.

It must be distinctly understood that by the Reichert method only a portion of the volatile fatty acids is recovered in the distillation process. The volatile fatty acids passing over consist, in the case of butter fat, in the main of butyric acid with which caproic, caprylic, and capric acids are admixed. In the case of coconut and palm-nut oils, butyric acid is absent, caproic and carpylic acids preponderating in the distillate. By filtering the distillate, caproic, caprylic, and capric acids are removed to the largest extent and are thus not accounted for in the Reichert-Wollny value.

Both Müntz and Coudon in France and Polenske in Germany extended the Reichert process by introducing a method for the approximate determination of the *insoluble* volatile fatty acids which pass over in the Reichert distillation process. Thus, after the Reichert-Meissl value has been determined, subsequently a second important value, affording a measure of the *insoluble volatile acids*, may be ascertained.

In the determination of this new value, the greatest attention must be paid to minute details and especially to the form of apparatus employed. Whereas Müntz and Coudon's apparatus is confined to France, Polenske's method has found application in this country, especially for the reason that this method closely followed the Reichert-Wollny process, and is in fact carried out in conjunction with it and in one and the same apparatus. As this method affords one of the best means of detecting coconut and palm-kernel oils in butter fat and in margarine, it is now in general use.

Polenske saponifies 5 grams of filtered (butter) fat, by the Leffmann-Beam process, with 20 grams of glycerol and 2 c.c. of sodium hydroxide solution (prepared from equal parts of sodium hydoxide and water) in a 300 c.c. flask by heating over a free flame. The solution is allowed to cool below 100°, 90 c.c. of water are added, and the mass dissolved by warming on the water-bath to about 50°. The solution must be clear and almost colourless. Should a brown solution be obtained, the test must be rejected. Fifty c.c. of dilute sulphuric acid (containing 25 c.c. of pure concentrated sulphuric acid in 1000 c.c.) and some *powdered* pumice are added to the hot soap solution; the flask is then immediately attached to the condenser. The apparatus to be employed must correspond in all details with the dimensions given in Fig. 4. The heat must be so regulated that within 19 to 20 minutes 110 c.c. are distilled off; the cooling water must be supplied at such a rate that the distillate does not drop into the 110 c.c. flask at a higher temperature than 20° to 23°. As soon as 110 c.c. have distilled over, the distillation is interrupted, the flask is removed, and is replaced by a 20 c.c. measuring cylinder.

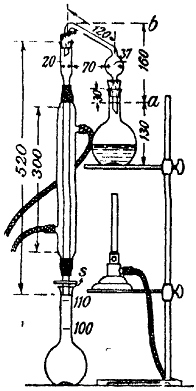


FIG. 4.

The distillate, which must not be shaken up, is immersed almost completely in water at 15°. After about 5 minutes the neck of the flask is slightly tapped, so that the oily drops floating on the surface may adhere to the walls of the flask. After a further 10 minutes, the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a solid (semi-solid) mass or oily drops. The contents of the flask are then mixed by turning the corked flask four or five times upside down, avoiding, however, violent shaking. 100 c.c. are filtered off through a filter of 8 cms. diameter, and titrated with decinormal caustic potash, as is done in the determination of the Reichert-Meissl value. In order to remove the soluble acids completely, the insoluble volatile acids on the filter are washed three times in succession with 15 c.c. of water, which have been passed severally through the tube of the condenser, the 20 c.c. measuring cylinder, and the 110 c.c. flask. These wash-waters are thrown away. In order to collect the insoluble volatile acids adhering to the tube of the condenser, the measuring cylinder, and the 110 c.c. flask, these vessels are rinsed three times in succession with 15 c.c. of neutralised 90 p.c. alcohol, and the alcoholic washes poured through the filter, each quantity being allowed to drain before a fresh wash is poured on the filter. The alcoholic filtrate is then titrated with decinormal alkali. The figure thus obtained has been termed ‘new butter value’ or ‘Polenske value,’ but the author prefers the term *titration number of insoluble volatile acids*, a term which has been adopted in France and Belgium. The titration value of the insoluble volatile acids lies in the case of butter fats as a rule between 2 and 4, in the case of coconut oil between 15 and 20, and in the case of palm-kernel oil between 10 and 12. (For a full discussion of this ‘value,’ *see* Lewkowitsch’s Chem. Techn., and for its relationship to other tests, *see* MARGARINE.)

Acetyl Value.

The acetyl value indicates the number of milligrams of potassium hydroxide (KOH) required for the neutralisation of the acetic acid obtained on saponifying one gram of an acetylated oil or fat.

The determination of the acetyl value of oils and fats is based on the principle that glycerides containing hydroxylated fatty acids assimilate, on being heated with acetic anhydride, one or more acetyl groups, according to whether the fatty acids contain one or more alcoholic hydroxyl groups. The chemical change consists in the replacing of the hydrogen atom of the alcoholic hydroxyl group or groups by the radicle of acetic acid, as explained by the following equations :—

$$\underset{\text{Ricinolein.}}{C_3H_5[O\cdot C_{18}H_{32}O(OH)]_3}+\underset{\text{Acetic anhydride.}}{3(C_2H_3O)_2O}$$

$$=\underset{\text{Acetyl ricinolein.}}{C_3H_5[O\cdot C_{18}H_{32}O(O\cdot C_2H_3O)]_3}+\underset{\text{Acetic acid.}}{3C_2H_4O_2}$$

$$\underset{\text{Sativin.}}{C_3H_5[O\cdot C_{18}H_{31}O(OH)_4]_3}+\underset{\text{Acetic anhydride.}}{6(C_2H_3O)_2O}$$

$$=\underset{\text{Tetra-acetyl sativin.}}{C_3H_5[O\cdot C_{18}H_{31}O\cdot(O\cdot C_2H_3O)_4]_3}+6H_2O$$

The determination of the acetyl value (first proposed by Benedikt) is carried out in the form given to it by Lewkowitsch : 10 grams, or any other convenient quantity, are boiled with twice the amount of acetic anhydride for 2 hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 to 600 c.c. of boiling water and heated for half an hour, while a slow current of carbon dioxide is passed into the liquid through a finely drawn-out tube reaching nearly to the bottom of the beaker ; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is siphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed ; this is ascertained by testing with litmus paper. Prolonged washing beyond the required limit causes slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter-paper, and dried in an oven to remove water.

About 5 grams of the acetylated product are then saponified by boiling with alcoholic potassium hydroxide solution, as is done in the determination of the saponification value. If the ‘distillation process’ be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic alkali. In case the ‘filtration process’ be used, the alcoholic potassium hydroxide solution must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated off and the soap dissolved in water. From this stage onwards, the determination is carried out either by (*a*) the distillation process, or (*b*) the filtration process.

(*a*) *Distillation process.*—Add dilute sulphuric acid (1 : 10), more than is required to saturate the alkali used, and distil the liquid in a current of steam ; 600–700 c.c. of water are distilled off. As a rule, this will be quite sufficient, and the last 100 c.c. will be found to require no more than 0·1 c.c. of decinormal alkali. Then titrate the distillate with decinormal potassium hydroxide solution, using phenolphthalein as an indicator, multiply the number of c.c. by 5·61. and divide by the weight of substance taken. This gives the *acetyl value.*

(*b*) *Filtration process.*—Add to the soap solution a quantity of standardised sulphuric acid, exactly corresponding to the amount of alcoholic alkali employed, and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potassium hydroxide.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*).

Both methods give identical results ; the latter requires less time and will, therefore, be found more convenient. The distilled water used in determining this value by either the distillation or filtration process must be carefully freed from carbonic acid by previous boiling, as otherwise serious errors ensue.

Pure triglycerides containing no hydroxylated acids have no acetyl value ; pure glycerides of hydroxylated fatty acids yield acetyl numbers which are in complete agreement with theory. In these cases, the acetyl value is a ‘characteristic.’ In the case of triglycerides containing, in addition to hydroxylated fatty acids, soluble acids as well, the acetyl value determined as described above would, of course, include soluble acids. The ‘apparent’ acetyl value obtained in such a case must, therefore, be diminished by the amount of alkali required for the saturation of the soluble fatty acids in order to obtain the *true* acetyl value. The amount of alkali required for the saturation of the soluble volatile acids must be ascertained by a blank test. Since acetyl values are also furnished by mono-glycerides and diglycerides (occurring in oils and fats having notable acid values), by free alcohols (such as phytosterol), and oxidised acids, and since all these substances occur in varying amounts in natural oils and fats, especially in those which have been exposed to the atmosphere and have become rancid, the acetyl value must, in these cases, be considered a ‘variable.’

Holland (J. Ind. Eng. Chem. 1914, 6, 482) suggests that, to make the value comparable with other values in fat analyses, the acetyl value should indicate the number of milligrams of potassium hydroxide required to saponify the acetyl taken up by 1 gram of fat on acetylation. He describes a simple method of determining the value

B. Variables.

1. *Acid Value.*

The acid value indicates the number of milligrams of potassium hydroxide required to saturate the free fatty acids in one gram of an oil or fat; or, in other words, it gives the amount of potassium hydroxide, expressed in tenths per cent., necessary to neutralise the free fatty acids in an oil or fat. This value is therefore a measure of the free fatty acids in an oil or fat.

For the determination of the acid value of an oil or fat, about 5 grams of a sample (if available) are mixed with neutral or neutralised alcohol (purified methylated spirit) and titrated with aqueous or alcoholic potassium hydroxide or sodium hydroxide solution, phenolphthalein being used as an indicator.

Example.—Weighed off 3·254 grams of tallow. Required for neutralising the free fatty acids 3·5 c.c. of decinormal potassium hydroxide (or soda) or 3·5×5·61 milligrams KOH. The amount of KOH required for 1 gram of tallow, *i.e.* its acid value, is therefore

$$A=\frac{3{\cdot}5\times5{\cdot}61}{3{\cdot}254}=6{\cdot}03$$

The acid value is frequently expressed in per cent. of oleic acid. Since the molecular weight of oleic acid, 282, is approximately five times 56·1 (the molecular weight of KOH), and the acid value expresses the amount of KOH in tenths per cent., a rapid and in most cases sufficiently accurate method of converting the acid value into per cent. of oleic acid is to multiply the former by 0·5. In the case of coconut oil and palm-kernel oil fatty acids this procedure would not be applicable, as their mean molecular weight lies, as a rule, between 210–220.

2. *Glycerol.*

If natural oils and fats represented neutral triglycerides, it would be possible to calculate the amount of glycerol obtainable on saponification from the following equation:

$$C_3H_5(OR)_3+3KOH=C_3H_8O_3+3KOR.$$

In the case of pure triglycerides, the proportion of glycerol obtainable being a 'characteristic' (see GLYCERIN), the quantity of glycerol yielded by an oil or fat can be calculated from the saponification value. In the case of natural oils and fats, a calculation of this kind will lead to erroneous results, not only on account of the (small) quantity of 'unsaponifiable matter' that is always present, but chiefly on account of the free fatty acids and mono- and di-glycerides which occur in natural oils and fats in variable quantities. Therefore, in the case of natural oils and fats, the percentage number of glycerol must be looked upon as a 'variable.'

This 'variable' stands in that general relation to the acid value that the higher the acid value, the smaller the yield of glycerol.

In order to determine the proportion of glycerol which an oil or fat yields on saponification, it is best to apply the 'acetin process' (*see* GLYCERIN) after a 'crude glycerin' has been prepared in the following manner:—

Twenty grams of the oil or fat are saponified (as described under *Saponification value*) with alcoholic potassium hydroxide solution, and the alcohol is driven off on a water-bath. The resulting soap is decomposed with sulphuric acid and the liberated fatty acids are filtered off. The filtrate is neutralised with an excess of barium bicarbonate and boiled down on the water-bath until most of the water has been driven off. The residue is exhausted with a mixture of ether and alcohol, the ether-alcohol driven off, for the most part, by gently heating on the water-bath, and the residue then left is dried in a desiccator and weighed. It is not necessary to dry until constant weight is obtained, as the actual glycerol present is determined in the crude product by the acetin method.

3. *Determination of the Unsaponifiable Matter.*

The author comprises under the term 'unsaponifiable matter' all those substances that are insoluble in water, or do not combine with alkali hydroxide to form soluble soaps. Most oils and fats contain, in their natural state, small quantities of unsaponifiable matter which consists to a great extent either of phytosterol in the case of vegetable oils and fats, or of cholesterol in the case of animal oils and fats. Other alcohols and hydrocarbons represent the smaller part of the 'unsaponifiable matter.'

Preparatory to the determination of the unsaponifiable matter, the oil or fat must be saponified as described above under *Saponification value*. In many cases it will, therefore, be found convenient to combine the determination of the saponification value with that of the unsaponifiable matter. But the amount of oil or fat taken should not be less than 5 grams. The unsaponifiable matter is determined as follows:—

Saponify 5 grams of the sample with 25 c.c. of double normal alcoholic potassium hydroxide solution in a flask under a reflux condenser and evaporate off the bulk of the alcohol. The residual soap is dissolved in 50 c.c. of hot water, and transferred to a separating funnel of about 200 c.c. capacity, using about 20–30 c.c. of water for rinsing the dish. After cooling, add 30–50 c.c. of ether and shake the solution thoroughly. Addition of a little alcohol will accelerate the separation. The soap solution is then run off into another separating funnel and is again exhausted with fresh ether. As a rule, two extractions will suffice; it is, however, safer to extract a third time. The ethereal solutions are united, washed with a small quantity of water to free them from any dissolved soap, and transferred to a tared flask. The ether is distilled off on the water-bath, and the residue dried at 100° and weighed.

In the case of most oils and fats ether should be preferred to petroleum spirit (which is largely used on the Continent). In order to counteract the property of petroleum spirit to dissolve alkaline soaps, the petroleum layer holding the unsaponifiable matter in solution should be washed with 50 p.c. alcohol instead of with water.

The above method must not be used in the case of oils and fats which have admixed with them vegetable or animal waxes, as the alkali salts of the fatty acids are not readily soluble in water or even in dilute alcohol. In such cases, it is best to neutralise the soap solution with acetic acid, with phenolphthalein as an indicator, and to precipitate with barium chloride or lead acetate. The residue is then washed, dried, mixed with sand and extracted in a Soxhlet apparatus with petroleum spirit boiling below 80°. If it be desirable to ascertain whether cholesterol or phytosterol or both, or animal or vegetable waxes or mineral oils, &c., be present, the unsaponifiable matter should be prepared in sufficient quantity to admit of further examination (*see* below *Examination of the Unsaponifiable Matter*)

(b) *Qualitative Methods.*

A large number of qualitative methods which were formerly in vogue, such as the elaïdin test, the sulphur chloride test, the thermal reactions with sulphuric acid (Maumené test), bromine or sulphur chloride, have been practically superseded by the determination of the iodine value. Inasmuch as the latter yields the same information in a more reliable and less ambiguous fashion than the tests enumerated, they need not be described here. (For a description of these methods, *see* Lewkowitsch, vol. i.) More important are the qualitative methods described below, inasmuch as they frequently furnish important data for the recognition of some oils and especially as they are usable for the valuation thereof. In cases where the quantitative methods do not supply full information the qualitative methods may be applied with advantage. The following qualitative methods are described here:—

(1) Oxygen absorption test.
(2) Bromide tests.
(3) Colour tests.

(1) Oxygen Absorption Test.

The absorption of oxygen from the atmosphere has a very important bearing on the liability of oils to cause spontaneous combustion when spread in a finely divided state on fibrous organic substances (*see* Wool oils). It is also of very great importance in the industries of paint oils, boiled oils, and varnishes.

It has been pointed out already that the iodine absorption of oils and fats stands in close relationship to the absorption of oxygen, and that the latter property, being a measure of the drying power of oils, was formerly used for purposes of classification. It has also been explained that the classification based on the iodine value includes the subdivision of oils into drying, semi-drying, and non-drying oils.

If a convenient method were known for the accurate determination of the oxygen which is absorbed during the drying process, it would be possible to class the determination of the drying power, or, as it might be termed, the 'oxygen value,' among the quantitative tests.

Determinations by earlier observers were made in a very unsystematic fashion, insufficient regard having been paid to such important factors as temperature, influence of light, moisture of the atmosphere, thickness of layer exposed, age of the oil, &c.

Since the drying of an oil requires a protracted length of time, attempts were made to accelerate the process of drying by mixing with the oils finely divided lead (Livache) or finely divided copper (Huebl; Lippert). Livache's lead powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying *in vacuó*. The test is carried out as follows: Spread about 1 gram of lead (or copper) powder, weighed off accurately on a somewhat large watch-glass, in a thin layer, and allow to fall on to it from a pipette 0·6 to 0·7 grams (not more) of the oil to be tested, placing each drop separately on the lead (or copper) powder, taking care that the drops do not run into one another. Then allow the watch-glass to stand at the ordinary temperature exposed to light.

In this process, linseed oil reaches the maximum absorption within a few days, whereas under ordinary conditions the same result is only arrived at after a much longer time has elapsed. Livache states that drying oils absorb the maximum quantity of oxygen after 18 hours, or, in some cases, after three days, whereas non-drying oils do not gain in weight before the lapse of four or five days. Weger condemns Livache's process, and recommends that larger quantities of lead should be used, so that for 0·2 grams of oil there should be taken at least 2 grams of lead powder. But even in that case the results were not found to be satisfactory.

Lippert, as also Weger, undertook a systematic study of the drying power of oils, by exposing them in very thin layers on glass plates to the action of the atmosphere. It was found that glass could not be replaced by any other material lighter in weight; thus celluloid, gelatin, and even ebonite were found useless. Sheets of mica, although useful for the work, are too easily damaged, and even sheets of thin metals have the drawback of being too easily creased. Necessary precautions in this test are: that the glass be perfectly clean, free from dust, and that the oil be spread with the greatest possible care in an evenly thin layer. If the layer is of uneven thickness, increase of weight might occur at one place, whilst simultaneously in a thinner layer loss of weight might take place. A series of experiments showed that the thinner the layer of oil exposed, the more rapidly is oxygen absorbed at the commencement of the experiment, but after 24 hours an equilibrium seems to be established. The thicker the layer the smaller is the increase, but if the layer is too thin, unreliable results will be obtained. The best conditions seem to be reached by spreading the oil so that about 0·0005 gram is used per square cm. of a glass plate (*see also* Linseed oil).

The process is an extremely tedious one, and depends on the accuracy with which decimilligrams can be ascertained. Besides, the method does not yield absolute values, and can only be used as a guide in comparative tests. It must, however, depend on the given circumstances whether this process should be applied. For if it is merely a question of discriminating between drying, semi-drying, and non-drying oils, the iodine value will not only be the most convenient sorting test, but will, at the same time, furnish quantitative results. It should be noted, however, that the iodine value must not be accepted as tantamount to defining the drying power. To take a striking example, fish and liver oils absorb approximately as much iodine as do the best drying oils, and yet they are greatly inferior to the latter as regards oxygen absorption power. Furthermore, fish and liver oils differ most materially from the 'drying oils,' in that they do not form a skin as does linseed oil (*see also* LINSEED OIL).

Fish and liver oils are best differentiated from the drying oils by the insoluble bromide test.

(2) Bromide Test.

Hehner and Mitchell devised a test conveniently applied in the following manner, which embodies some modifications worked out in the author's laboratory: Dissolve 1 to 2 grams of oil in 40 c.c. of ether, to which a few c.c. of glacial acetic acid have been added, cool the solution in a corked flask to 5°, and add bromine drop by drop until the brown coloration remains permanent. If the temperature were allowed to rise too high, evolution of hydrogen bromide would become noticeable; in that case, the experiment must be repeated. After standing for 3 hours at a temperature of 5°, the liquid is passed through a filter, and the precipitate, consisting probably of the bromide of a mixed glyceride, is washed four times in succession, using each time 10 c.c. of chilled ether. The residue is finally dried in a water-oven to constant weight. In the following table a number of experiments are collated which have been carried out by Hehner and Mitchell, by the author and by his assistants Walker, Warburton, and Stadler.

Kind of oil	Yield of insoluble bromides from glycerides per cent	Observer
Linseed (iodine value 181) .	23·14; 23 52	Walker and Warburton
Linseed (iodine value 186·4) .	24 17	Lewkowitsch
Linseed (iodine value 190 4) .	37·72	,,
Linseed . .	23 86–25 8	Hehner and Mitchell
Tung . .	nil	,, ,,
,, I. . .	nil	Walker and Warburton
,, II. . .	0·38; 0·39	,, ,,
Candle nut .	8·21; 7·28	,, ,,
Walnut . .	1·42–1·9	Hehner and Mitchell
Safflower . .	0 65–1·65	Walker and Warburton
Poppy seed	nil	Hehner and Mitchell
Soya-bean oil .	5·0	Lewkowitsch
Maize . .	nil	Hehner and Mitchell
Cotton seed .	nil	,, ,,
,, ,, cooled	nil	Lewkowitsch
Rape oil . .	3·0	Stadler
Brazil nut .	nil	Hehner and Mitchell
Almond . .	nil	,, ,,
Olive . .	nil	,, ,,
Japan fish .	21·14; 22·07	Walker and Warburton
Fish, deodorised	49·01; 52·28	,, ,,
Cod liver. .	42·9	Hehner and Mitchell
,, ,, . .	35·33; 33·76	Walker and Warburton
,, Newfoundland	32·68; 30·62	,, ,,
Shark liver .	22·0	Hehner and Mitchell
,, ,, .	21·22; 19·08	Walker and Warburton
Seal . .	27·54; 27·02	,, ,,
Whale . .	25·0	Hehner and Mitchell
,, old sample	15·54; 16·14	Walker and Warburton
,, fresh sample	20·1–22·6	Lewkowitsch
Sperm . .	2·61; 2·42	Walker and Warburton

In the author's opinion, derived from very extensive practice with this method, it is preferable to apply the 'bromide test' to the isolated fatty acids (*see* below).

(3) Colour Tests.

Very many colour reactions have been proposed from time to time, and are still being proposed, for the recognition of individual oils.

Colour reactions were chiefly resorted to for lack of better methods; they have been superseded in the majority of cases by the 'quantitative reactions.' It should be borne in mind that many colour reactions quoted in older textbooks, and perpetuated even in more modern treatises, were not always obtained with typical samples, little or no regard having been paid to their source, their mode of purification, their age, and all that variety of circumstances which influences the colour produced by the reagents. In consequence of progress made in technical processes, a large number of impurities, which were in fact the very substances that gave origin to the colours supposed to be characteristic of the oils or fats, has ceased to occur in commercial samples.

A colour reaction can only be considered of some value if it be produced by a well-defined substance, occurring naturally in an oil or fat, and characteristic of it to such an extent that the sample may be identified by that reaction. Obviously, these characteristic substances which only occur in minute quantities should not be easily removable in the course of the usual manufacturing processes.

An extensive inquiry made by the author (J. Soc. Chem. Ind. 1894, 617, and Chem. Techn.) into the colour reactions, has led him to conclude that only the following tests can be considered:—

Baudouin's test.—This test, originally proposed by Camoin, is indicative of sesamé oil, inasmuch as a substance which occurs in this oil gives with hydrochloric acid and sugar a characteristic red coloration. Since cane sugar yields lævulose and furfural, Villavecchia and Fabris proposed to carry out this test in the following manner, which can be thoroughly recommended:—

Place 0·1 c.c. of a 2 p.c. alcoholic furfural solution in a test-tube, add 10 c.c. of the oil to be tested, and 10 c.c. of hydrochloric acid of sp.gr. 1·19; shake the mixture for half a minute and allow it to settle. In the presence of sesamé oil, even if it be less than 1 p.c., the aqueous layer will acquire a distinct crimson colour. In the absence of sesamé oil, the lower layer is either colourless, or has at most (as in the case of a very rancid though pure olive oil) a dirty yellow colour. The great sensitiveness of this reaction has led to the compulsory ear-marking of margarine, in several continental countries, by the legally prescribed addition of 5–10 p.c. of sesamé oil to margarine. In case an oil or fat has already been coloured with a colouring matter furnishing a red coloration with hydrochloric acid alone (which not infrequently occurs in the case of margarine coloured with 'butter colour'), the colouring matter must be previously removed by frequent shaking out with concentrated hydrochloric acid. In many cases, however, the colouring matter contained in the sesamé oil is destroyed at the same time.

Halphen's colour test.—This test indicates cotton-seed oil and is carried out in the following manner: 1 to 3 c.c. of the oil is dissolved in an equal value of amyl alcohol; to this is added 1 to 3 c.c. of carbon disulphide holding in solution 1 p.c. of sulphur (flowers). The test-tube containing the mixture is then immersed in boiling water, and kept therein for some time. The carbon disulphide evaporates off; in the presence of cotton-seed oil a deep red coloration appears in the course of 5 to 15 minutes. This colour reaction is most characteristic; it is possible to detect thereby 5 p.c., and even less, of cotton-seed oil admixed with other oils and fats, *e.g.* olive oil or lard. In case the proportion of cotton-seed oil is very small, the test-tube must be kept in the water-bath for 20 to 30 minutes, or preferably in a salt-bath at 105°. Mixtures of olive and arachis oils containing 1 p.c. of cotton-seed oil, gave, in the author's laboratory, distinct colorations after 25 to 30 minutes. Over-estimation of this test must, however, be guarded against as, on the one hand, cotton-seed oil, which has been heated at 180°–250°, no longer yields the red coloration. On the other hand, it must be remembered that on feeding cows and pigs with cotton-seed cake, the chromogenetic substance passes into the milk fat of cows and into the lard. It must, also, be noted that no quantitative interpretation should be based upon the depth of the red coloration obtained, even if the presence of cotton-seed oil has been placed beyond doubt.

It should further be noted that kapok oil and baobab oil give the same colour reaction, the last-named oil with even greater intensity than cotton-seed oil.

Becchi's colour test.—This test is much less reliable than Halphen's test and is only described here because it is still largely used in the South of Europe (France, Italy). It is safest, if Becchi's test must be applied, to use it in the form suggested by Tortelli and Ruggeri: Five grams of the liquid fatty acids of the suspected sample are dissolved in 10 c.c. of alcohol, and 1 c.c. of a 5 p.c. silver nitrate solution is added; the sample is then heated on a water-bath at 70°–80°. Cotton-seed oil acids reduce the silver immediately, whereas the fatty acids of olive oil and other oils remain clear for some time. Even cotton-seed oils—which have been heated at 250° for 10 and 20 minutes respectively—can be recognised when present in as low a proportion as 10 p.c. in olive oil, on allowing the liquid acids of the mixed oil to stand in the hot water-bath for several hours.

Nitric acid test.—This test may be used in many cases for the preliminary identification of cotton-seed oil. The test is best carried out with nitric acid of 1·375 sp.gr. (Lewkowitsch). A few c.c. of the sample are shaken energetically with an equal measure of nitric acid of the specified gravity 1·375, and the sample is allowed to stand for some time, up to 24 hours. Cotton-seed oil gives a coffee-brown coloration which is characteristic of this oil to such an extent that admixtures of 10–12 p.c. of cotton-seed oil with olive oil can be detected in certain cases. But even here circumspection is necessary, as the coffee-brown coloration given by some specimens of cotton-seed oil is not characteristic of all cotton-seed oils. Of importance is the observation made by the author, viz. that a specimen of heated cotton-seed oil which no longer gives the Halphen test still gives a brown coloration with nitric acid, and also that the fatty acids from heated cotton-seed oil show the coloration distinctly.

It may be repeated that the last three colour tests, which are employed for the detection of cotton-seed oil, should only be used with the greatest circumspection. In any case they can only serve as preliminary or confirmatory tests.

Liebermann-Storch reaction.—This colour test is exceedingly reliable for the detection of rosin oils: 1 to 2 c.c. of the sample under examination are shaken, in a test-tube, with acetic anhydride at a gentle heat; after cooling, the acetic anhydride layer is drawn off by means of a pipette, and tested by adding one drop of sulphuric acid of 1·53 sp.gr. (This acid contains 62·53 p.c. of SO_4H_2; it is prepared by mixing 34·7 c.c. of concentrated sulphuric acid with 35·7 c.c. of water.) If rosin oil is present, a fine violet (fugitive) colour is immediately produced. If less than 1 to 2 c.c. are available, the test can be made on a watch-glass, by stirring the liquid with acetic anhydride and allowing a drop of sulphuric acid to run down the side. It should be borne in mind that cholesterol gives a similar colour reaction.

Sulphuric acid test.—All sulphuric acid colour reactions described in the older literature of this subject are unreliable with the exception of the test for liver oils. This is best carried out in the following manner: 1 drop of oil is dissolved in 20 drops of carbon disulphide and 1 drop of concentrated sulphuric acid is added. In the presence of liver oils, a beautiful violet-blue colour appears at once, changing afterwards into red and brown. It has been shown by Drummond and Watson (Analyst, 1922, 47) that the coloration is not due to lipo-chromes, but stands in some relationship to the vitamin content of the oil.

II. Examination of Fatty Acids.

In case the preceding methods, described under A. and B., have not furnished sufficient information for the identification of a specimen, it becomes necessary to examine the free fatty acids.

If great accuracy is required it is not permissible to examine the fatty acids as obtained by the decomposition of the soap solution—resulting on saponification of the oils and fats—as the separated fatty acids naturally retain the unsaponifiable matter. Rather is it necessary to remove the unsaponifiable matter previous to the decomposition of the soap solution by the methods described above.

A list of the natural fatty acids likely to be met with in the examination has been set out in the table, p. 647. It will be found convenient to have the few indications given above amplified by the following notes.

I. ACIDS OF THE ACETIC SERIES: $C_nH_{2n}O_2$.

These acids contain a normal chain and are best characterised for analytical purposes by their property of not absorbing any iodine, *i.e.* their iodine value is *nil*. The lowest members of the series are miscible with water in every proportion. The solubility in water decreases rapidly with the increase of the number of carbon atoms in the molecule. Capric acid is practically insoluble in cold water, somewhat more soluble in hot water. Lauric acid is very slightly soluble in boiling water. The higher acids are practically insoluble in water.

Taking solubility in water as a basis of classification, we may, for analytical purposes, subdivide these fatty acids into *soluble* and *insoluble* fatty acids. The acids up to caprylic acid are termed *soluble* fatty acids; the higher fatty acids, from myristic acid upwards, are the *insoluble* fatty acids. Capric and lauric acids occupy, also as regards solubility, an intermediate position. The lead salts of the higher fatty acids, commencing with palmitic acid, are insoluble in ether.

Acetic Acid *v.* Vol. I. p. 11.

Butyric Acid *v.* Vol. I. p. 718.

*iso***Valeric Acid** *v.* VALERIC ACID.

Caproic acid, $C_6H_{12}O_2$, discovered by Chevreul in 1818, is not miscible with water, although it is, to some extent, soluble in it, sp.gr. at 20°/4° is 0·924; n_D^{20} = 1·41635; its odour is like that of sweat: 100 c.c. of water dissolve 0·822 gram at 15°.

Methyl ester, sp.gr. 0·9309 at 0°; b.p. under 760 mm. pressure, 149·6°; under 15 mm. pressure, 52°–53°.

Ethyl ester, sp.gr. 0·8890 at 0°; sp.gr. 0·8732 at 20°; sp.gr. 0·8594 at 40°; b.p. 165·5°–166° under 735·8 mm. pressure.

Caprylic acid, $C_8H_{16}O_2$, discovered by Lerch (1844) in butter fat. sp.gr. 0·9270 at 0° and 0·9100 at 20°/40°; n_D^{20} 1·42825. One part dissolves in 400 parts of boiling water; the dissolved acid separates out almost completely on cooling: 100 c.c. of water at 15° hold in solution 0·079 gram of acid. The acid has an intense odour of sweat. It also occurs in the oils belonging to the coconut oil group.

Methyl ester, sp.gr. 0·8942 at 0°; sp.gr. 0·887 at 18°; solidifying point −40° to −41°; b.p. 192°–194° under 760 mm.; 95° under 25 mm., 83° under 15 mm. pressure.

Ethyl ester, sp.gr. 0·8842 at 0°; 0·8730 at 16°; solidifying point, −47° to −48°; b.p. 207°–208°.

Capric acid, $C_{10}H_{20}O_2$, like the foregoing two acids, is characteristic of the milk fats and the oils of the coconut group. It occurs in wool yolk as potassium salt. The acid crystallises in fine needles, sp.gr. 0·930 at 37°; 0·8858 at 40°; n_D^{40} 1·42855. It is almost insoluble in cold water; one part dissolves in about 1000 parts of boiling water. The acid has a goat-like smell, which becomes more distinct at the temperature of its melting-point.

Methyl ester, boils at 223°–224° under 760 mm. and at 114° under 15 mm., solidifies at −18°.

Ethyl ester, sp.gr. 0·862; b.p. 243°–245°.

Lauric acid, $C_{12}H_{24}O_2$, is characteristic of the oils of the coconut oil and dika fat groups. At the ordinary temperature the acid is solid, and crystallises from alcohol in needles. It is the first acid of the acetic series that cannot be distilled at ordinary pressure without undergoing (slight) decomposition: sp.gr. 0·883 at 20°/4°; 0·875 at 43·6°/4; 0·8642 at 60°/4°; n_D^{60} 1·42665; n_D^{76} 1·4236. Lauric acid is slightly soluble in large quantities of boiling water; on distilling its aqueous solution, it passes over to an appreciable extent with the vapours. The laurates of the alkali-metals differ from the corresponding salts of the higher fatty acids in that they require large quantities of salt for 'salting out' (*v.* SAPONIFICATION).

Methyl ester, b.p. 141° under 15 mm.; 148° under 18 mm.; m.p. +5°.

Ethyl ester, sp.gr. 0·8671 at 19°; solidifying point −10°; b.p. 269° under ordinary pressure.

Myristic acid, $C_{14}H_{28}O_2$, is characteristic of all the fats belonging to the *Myristica* group (*see* MYRISTICA FATS). It was discovered by Playfair in nutmeg butter. It is also stated to occur as cetyl myristate in spermaceti and, in combination with unknown alcohols, in wool wax. The acid crystallises in laminæ; sp.gr. 0·8622 at 53·8°/4°; 0·8584 at 60°/4°; n_D^{60} 1·43075; $n_D^{76·5}$ 1·4248; is completely insoluble in water; when boiled with water, about 7·7 p.c. is carried over with the vapour; it dissolves with difficulty in cold alcohol and ether.

Methyl ester, b.p. 167°–168° under 15 mm. pressure; m.p. 18°.

Ethyl ester, boils at 295° under ordinary pressure, and *in vacuô* at 102° or 124°; solidifies at 10·5°–11·5°; sparingly soluble in alcohol or ether, more readily soluble in light petroleum.

Palmitic acid, $C_{16}H_{32}O_2$, occurs in most vegetable and animal fats; and notably in large quantities in palm oil (from which it was first isolated in a pure state by Fremy); in Chinese vegetable tallow, Japan wax, and myrtle wax. It occurs also in spermaceti and in opium wax as ceryl palmitate, in beeswax as myricyl palmitate.

Palmitic acid has been prepared artificially on a large scale by melting oleic acid with caustic alkali, hydrogen being evolved; in addition to palmitic acid smaller quantities of oxalic and acetic acids are formed. This process has been abandoned as impracticable.

Palmitic acid forms tufts of finely crystalline needles; the melted acid solidifies on cooling to a nacreous, scaly, crystalline mass. It boils between 339° and 356° with slight decomposition; distils unchanged under a pressure of 100 mm. at 271·5°; under a pressure of 15 mm. at 215°, and *in vacuô* at 138°–139°. On a large scale it is distilled with the aid of superheated steam; sp.gr. 0·8527 at 62°/4°; 0·8412 at 80°/4°; $n_D^{74·5}$ 1·4284; n_D^{80} 1·42693. It is not readily soluble in cold alcohol; 100 c.c. of methylated alcohol (sp.gr. 0·8183) dissolve at 0° from 1·2 to 1·3 grams; 100 c.c. of 95 p.c. (by volume) alcohol hold in solution at 0°, 0·56 gram; 100 parts of absolute alcohol dissolve, at 19·5°, 9·32 parts. It dissolves very easily in boiling alcohol; petroleum spirit does not dissolve it very readily.

The metallic salts of palmitic acid resemble very closely those of stearic acid (*v. infra*), but they possess a somewhat greater solubility. Palmitic acid is determined quantitatively in palmitates by precipitating their solutions with hydrochloric acid, washing the precipitate with water, dissolving it in absolute alcohol or ether, evaporating to dryness, and finally drying in a desiccator over sulphuric acid.

Methyl ester, b.p. 196° under 15 mm. pressure; m.p. 28°.

Ethyl ester, b.p. 122° *in vacuô*; m.p. 24·2°.

Stearic acid, $C_{18}H_{36}O_2$, occurs very abundantly in many vegetable and animal fats, especially in the hard ones, such as cacao butter, shea butter, and tallow. The higher the melting-point of a fat, the higher is, as a rule, the proportion of stearic acid it contains. Stearic acid may be obtained synthetically by the reduction of less saturated acids, containing an open chain of 18 carbon atoms (oleic, linolic, linolenic, clupanodonic) by means of hydrogen in the presence of a suitable catalyst, such as nickel or palladium. It forms white, nacreous laminæ, melting at 69·32° to a perfectly colourless liquid which, on cooling, solidifies at 69·3° to a crystalline translucent mass; boils under ordinary pressure at about 360° with slight decomposition; *in vacuô* it distils unchanged. On a large scale it is distilled in a current of superheated steam without any decomposition. Under 100 mm. pressure it boils at 291°, under 15 mm. at 232°, and *in vacuô* at 154·5°–155·5°: sp.gr. 0·8454 at 69·2°/4°, 0·8386 at 80°/4°. At 11° its sp.gr. equals that of water; at more elevated temperatures it floats on water, as it expands more quickly than the latter: n_{D}^{80} 1·43003.

Like palmitic acid it possesses neither smell nor taste; it is greasy to the touch and produces a grease-spot on paper. Insoluble in water; in hot alcohol it dissolves easily; it is less soluble in absolute alcohol than palmitic acid, one part of stearic acid requiring 40 parts of alcohol. 100 c.c. of alcohol, sp.gr. 0·818 (at 15·5°) hold in solution, at 0°, 0·0814 gram, if the solution be prepared with about 3 grams of stearic acid, but owing to supersaturation, the dissolved amounts fluctuate considerably, depending on the amount of stearic acid used. Thus, with 7 grams of stearic acid, varying quantities of dissolved stearic acid from 0·0810 rising up to 0·1082, have been found (Lewkowitsch). Stearic acid dissolves easily in ether.

Potassium stearate, $KC_{18}H_{35}O_2$, forms crystals having a greasy lustre; dissolves in 6·6 parts of boiling alcohol. On diluting the hot aqueous solution with a large proportion of water, pearly laminæ of an acid stearate

$$KC_{18}H_{35}O_2{\cdot}C_{18}H_{36}O_2$$

separate. The salt is insoluble in ether, petroleum spirit, carbon disulphide, and chloroform. (Difference from potassium oleate.)

Sodium stearate, $NaC_{18}H_{35}O_2$, closely resembles the potassium salt. In the crystalline state it forms lustrous laminæ.

Ammonium stearate, $(NH_4)C_{18}H_{35}O_2$, loses part of its ammonia on being warmed in aqueous solution, and is converted into the acid salt. The same change takes place when the ammonia soap is allowed to stand over concentrated sulphuric acid in a desiccator.

Calcium, *strontium*, *and barium stearates* form crystalline precipitates, practically insoluble in alcohol. The insoluble salts are, to some extent, hydrolysed on washing with water. Thus barium stearate gives up to the water barium oxide, and free stearic acid (which can be extracted with alcohol) remains behind with the undissociated residue. The *magnesium* salt crystallises in microscopical laminæ; it is nearly insoluble in cold alcohol, but sufficiently soluble in boiling alcohol to allow it to be crystallised from its solution. The *lead* salt melts at 115°–116° without undergoing decomposition; it is very sparingly soluble in ether (difference from oleic acid), and still less in light petroleum. 50 c.c. of absolute ether dissolve 0·0074 gram of lead stearate. In hot benzene, lead stearate dissolves, but separates almost completely on cooling to 8°–12°. In absolute alcohol, lead stearate is very sparingly soluble. Stearic acid cannot be determined quantitatively by weighing its calcium or barium salts, a method which has been proposed repeatedly.

Methyl ester, b.p. 214°–215°; m.p. 38°.

Ethyl ester, boils *in vacuô* at 139° or 154°; it melts at 36·7°.

Arachidic acid, $C_{20}H_{40}O_2$, discovered by Goessmann (1854), occurs in notable quantities in arachis oil; it has also been found in butter fat. It crystallises in small lustrous scales, sparingly soluble in cold alcohol; dissolves easily in boiling alcohol. 100 parts of 90 p.c. alcohol dissolve at 15°, 0·022 parts, and at 20°, 0·045 parts of arachidic acid. It dissolves readily in ether, chloroform, petroleum spirit, or benzene.

Methyl ester, m.p. 54·5°.

Ethyl ester, b.p. 284°–286° under 100 mm. pressure; m.p. 50°.

Behenic acid, $C_{22}H_{44}O_2$, melts at 80°–82° and solidifies at 70°–76°. Synthetical behenic acid from erucic acid melts at 83°–84° and solidifies at 79°–77°. It boils under 60 mm. pressure at 306° and crystallises in needles; it is less soluble in alcohol than in ether. 100 parts of alcohol dissolve, at 17°, 0·102 gram; 100 parts of ether, at 16°, 0·1922 gram.

Ethyl ester, m.p. 48°–49°.

Lignoceric acid, $C_{24}H_{48}O_2$, occurs in arachis oil, in association with arachidic acid; crystallises from alcohol in white flocks of silky lustre, which become scaly and show nacreous lustre when pressed between filter-paper; sparingly soluble in cold alcohol, dissolves readily in benzene, ether, or carbon disulphide.

Methyl ester, m.p. 56·5°–57°.

Ethyl ester, m.p. 55°; distils without undergoing decomposition at 305°–310° under a pressure of 15–20 mm.

II. ACIDS OF THE ACRYLIC OR OLEIC SERIES: $C_nH_{2n-2}O_2$.

These acids absorb two atoms of halogen from Hübl's or Wijs' iodine solution. By means of hydrogen, in the presence of a catalyst, they are readily reduced to the corresponding acids of the acetic series. By oxidation with a dilute solution of potassium permanganate in alkaline solution, the unsaturated acids are converted into the corresponding saturated hydroxylated acids (*v. infra*). On melting with caustic alkalis, they are broken up into lower acids; thus oleic acid yields palmitic, acetic, and other acids. During this reaction, a migration of the double linkage takes place. Some of the higher acids, notably oleic and erucic acids, are changed into crystallisable isomerides when treated with a small quantity of nitrous acid at the ordinary temperatures, or with sulphurous acid or bisulphites at high temperatures and under pressure.

The unsaturated acids are more readily soluble in alcohol than the saturated acids having the same number of carbon atoms. The lead salts of these acids are readily soluble in ether, with the exception of erucic acid, which dissolves only with difficulty in cold ether.

Ozone is readily assimilated by oleic acids, forming perozonides, which are easily converted into the more soluble ozonides (*see* Lewkowitsch, Chem. Techn. [i.]).

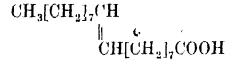
The action of concentrated sulphuric acid or anhydrous zinc chloride on the higher members of this series is a very complicated one (*v. infra* and also SAPONIFICATION).

Tiglic acid, $C_5H_8O_2$ (an isomeride of angelic acid), occurs in croton oil, crystallises in triclinic columns, melting at 64·5°, and boiling at 198·5° under ordinary pressure; sp.gr. 0·9641 at 76°.

Hypogaeic acid, $C_{16}H_{30}O_2$, has been stated to occur naturally in arachis oil. It has been prepared synthetically from stearolic acid and crystallises in needles melting at 33°–34°, boiling at 236° under a pressure of 15 mm., and at 230° under a pressure of 10 mm. By nitrous acid it is converted into *gaidic acid*.

Oleic acids. Theory predicts a number of different 'oleic acids,' according to the position which the doubly linked carbon atoms occupy in the molecule, quite apart from stereo-isomerides obtained by the action of nitrous acid on the several 'oleic acids.' Here only the more important members of this group can be described.

(*a*) **Ordinary Oleic acid**



$$\begin{array}{l} CH_3[CH_2]_7CH \\ \qquad\qquad \| \\ \qquad\qquad CH[CH_2]_7COOH \end{array}$$

is found in most vegetable and animal fats, especially in the liquid ones, in combination with glycerol. Pure oleic acid is best prepared from tallow (which does not contain notable quantities of less saturated acids than oleic acid), by saponifying with potassium hydroxide, precipitating the soap solution with lead acetate, and extracting the dried lead salt with ether. The dissolved lead salt is decomposed by hydrochloric acid under ether, the liberated acid dissolved in ammonia, and the solution treated with barium chloride. The barium salt is dried, dissolved in hot alcohol, and the hot solution allowed to crystallise. The crystallised salt is decomposed either by strong mineral acid or by tartaric acid. The acid so prepared still contains some palmitic and stearic acids, owing to the solubility of the lead salts of the solid acids in the ethereal solution of lead oleate.

Pure oleic acid is a colourless liquid free from odour. It crystallises in the form of needles, solidifying at 4°, and melting at 6·5°; an allotropic form melts at 16°. Sp.gr. 0·898 at 14°; or 0·8908 at 11·8°/4, 0·898 at 15°, 0·895 at 20°, 0·889 at 30°, 0·875 at 50°, 0·854 at 78·4°.

On distilling oleic acid under ordinary pressure, it is partially broken up into water, and into carbonic, acetic, caprylic, and capric acids; at the same time, sebacic acid and hydrocarbons are formed. In a current of superheated steam, however, it passes over unchanged at a temperature of about 250°. This is, indeed, the method by which oleic acid is prepared on a manufacturing scale in candle-works. It is insoluble in water, dissolves readily in cold alcohol, even if the alcohol be somewhat dilute. On adding large quantities of water to the alcoholic solution, the acid is thrown out.

Nitrous acid, at the ordinary temperature converts oleic acid into elaidic acid. The same change takes place when the acid is treated with sodium bisulphite under pressure at 175°–180°, or with sulphurous acid, under pressure, at 200°. The change, however, is not complete, as the reaction is a reversible one.

On blowing air through oleic acid at 120° for 2, 4, 6, and 10 hours, the author obtained respectively 0·62, 2·6, 3·5, and 6 p.c. of 'oxidised' acids, insoluble in petroleum spirit (*v. infra*); the specific gravities of the products rose in the same order from 0·8980 to 0·9098, 0·9121, 0·9123, and 0·9238 respectively. Similarly, on digesting oleic acid with sulphur at a temperature between 130° and 150°, sulphur is absorbed, without evolution of sulphuretted hydrogen; apparently an addition-product is formed. At higher temperatures, from 200°–300°, sulphuretted hydrogen is evolved.

Oleic acid dissolves in concentrated sulphuric acid in the cold, and forms stearic-acid-hydrogen sulphate, $C_{18}H_{35}(SO_4H)O_2$; on boiling this product with water, sulphuric acid is split off and ι-hydroxystearic acid is formed conjointly with a small quantity of stearolactone (Geitel), (*see* SAPONIFICATION). A similar change takes place on heating oleic acid with zinc chloride to 185°. By the catalytic reduction of oleic acid with hydrogen, oleic acid is converted quantitatively into stearic acid (*see* Lewkowitsch, J. Soc. Chem. Ind. 1908, 489).

Sodium oleate, $NaC_{18}H_{33}O_2$. The pure salt is prepared by crystallisation from absolute alcohol (not from dilute alcohol). It dissolves in 10 parts of water at 12°, or in 20·6 parts of alcohol, sp.gr. 0·821 at 13°. It also dissolves in 100 parts of boiling ether. The anhydrous salt melts at 232°–235°.

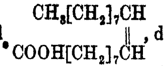
Potassium oleate, $KC_{18}H_{33}O_2$, forms a transparent, jelly-like mass, which is far more readily soluble in water, alcohol, and ether than the sodium salt. One part of the salt requires for complete solution 4 parts of water, or 2·15 parts of alcohol, or 29·1 parts of boiling ether.

Ammonium oleate, $NH_4C_{18}H_{33}O_2$, forms 'liquid crystals.'

The metallic oleates are mostly soluble in alcohol, benzene, chloroform, carbon tetrachloride, carbon disulphide, nitrobenzene, pyridine, or petroleum spirit; some oleates are also soluble in ether.

Methyl ester, sp.gr. 0·879 at 18°; boils under a pressure of 15 mm. at 212°–213°.

Ethyl ester, sp.gr. 0·871 at 16°.

(*b*) **Elaïdic acid** 

$$\begin{array}{l}CH_3[CH_2]_7CH\\ \qquad\qquad\quad\ \ \|\\ COOH[CH_2]_7CH\end{array}$$

, discovered by Boudet (1832), is obtained by allowing nitrous acid fumes, or a nitrite and nitric acid, to act on oleic acid at the ordinary temperature; after a short time, the oleic acid is changed into its stereoisomeride, elaïdic acid. The separation of elaïdic acid from the unchanged oleic acid is readily effected by crystallisation from alcohol or ether, or by separating the lead salts by means of ether or benzene. It crystallises from alcohol in plates, melting at 44·5°; sp.gr. 0·8505 at 79·4°/4°. It can be converted, in its turn, into ordinary oleic acid by boiling iodostearic acid, prepared from elaïdic acid, with alcoholic potash; simultaneously some '*iso*-oleic' acid is formed.

(*c*) *iso***Oleic acid** (**Para-oleic**), **Solid Oleic acid**, was described as an individual acid by M., C., and A. Saytzeff and was prepared by distilling ι-hydroxystearic acid under diminished pressure, when a mixture of ordinary oleic and '*iso*-oleic' acids, together with some unchanged hydrostearic acid, passed over.

The constitution $CH_3[CH_2]_{14}CH{=}CH{\cdot}COOH$ ascribed to this acid, has been shown to be erroneous. Arnaud and Pasternak (Compt. rend. 150, 1525) state that '*iso*-oleic' acid is not an individual, but represents a mixture of several acids from which hitherto the ordinary 9 : 10-elaïdic acid, the ordinary 9 : 10-oleic acid, an 8, 9-elaïdic acid, and a hydroxystearic acid, $C_{18}H_{36}O_3$, could be isolated, but these acids do not yet exhaust the number of acids occurring in the mixture hitherto considered as '*iso*-oleic' acid.

(*d*) **Rapic acid**, $C_{18}H_{34}O_2$, is the 'oleic acid' occurring in rape oil; it does not solidify on cooling, nor does it yield a solid isomeride when acted upon with nitrous acid.

Erucic acid, $C_{22}H_{44}O_2$, discovered by Darby (1849), occurs in the oils belonging to the rape-oil group. The acid crystallises from alcohol in long fine needles. Erucic acid resembles ordinary oleic acid in its properties; thus it is converted by nitrous acid into its stereoisomeride, *brassidic acid*; it is reduced by suitable treatment to the saturated behenic acid. On being melted with potassium hydroxide it splits up into acetic and arachidic acids.

'*isoErucic*' acid is obtained by boiling iodobehenic acid with alcoholic potash. No doubt this acid, like *iso*-oleic acid, will be found to consist of a mixture of acids.

III. Acids of the Linolic Series: $C_nH_{2n-4}O_2$.

The acids belonging to this series are characterised by their property of absorbing four atoms of halogen, or two molecules of iodochloride. Hence these acids must be looked upon as containing two pairs of doubly-linked carbon atoms. They readily absorb oxygen on exposure to the air; this important property is made use of in the arts (*Drying oils*). They assimilate two molecules of ozone. On oxidation with potassium permanganate solution in the cold they yield tetrahydroxylated acids (*v. infra*). Nitrous acid does not convert them into solid isomerides. By suitable treatment with hydrogen they are converted into acids of the saturated series. It appears, therefore, that the acids belonging to this series are open chain acids.

Linolic acid, $C_{18}H_{32}O_2$, occurs in considerable proportions in drying and semi-drying oils. Pure linolic acid was obtained by saponifying its methyl ester. The acid is a colourless oily liquid, sp.gr. 0·9026 at 18°. On brominating linolic acid, a crystalline tetrabromide $C_{18}H_{32}O_2Br_4$, melting at 114°–115°, is obtained. On oxidising linolic acid with a dilute solution of potassium permanganate in the cold, tetrahydroxystearic (sativic) acid, $C_{18}H_{36}O_6$, melting at 173°, is formed. According to Erdmann and Bedford, there exist an α- and a β-linolic acid, the latter of which yields a liquid tetrabromide. The formation of the crystalline tetrabromide permits of the detection and also approximate quantitative determination of linolic acid (*see* Linseed oil).

Several other 'linolic acids' differing from the ordinary linolic acid by their yielding different tetrabromides and tetrahydroxystearic acids have been described. Thus *telfairic acid* yields a tetrabromide, melting at 57°–58°, and a tetrahydroxystearic acid, melting at 177°.

Elæomargaric acid, $C_{18}H_{32}O_2$

$CH_3[CH_2]_3CH:CH[CH_2]_2CH:CH[CH_2]_7COOH$

(*Majuna*), crystallises in rhombic plates, melting at 43°–44°. It absorbs oxygen readily from the air and is thereby converted into a resinous mass. In an alcoholic (or ethereal) solution the acid remains unchanged if protected from light. On exposure to light, however, crystals melting at 71° are deposited from the alcoholic solution. These crystals have the same composition as elæomargaric acid. According to Maquenne, the higher melting acid, termed by Cloez elæostearic acid, is a stereoisomeride of elæomargaric acid, and stands to it in the same relationship as does elaïdic acid to oleic acid. On bromination it yields a tetrabromide, which is identical with the solid tetrabromide obtained from linolic acid. On oxidising elæomargaric acid with potassium permanganate, Kametaka obtained dihydroxystearic acid, and also azelaïc acid and an unknown crystalline substance melting at 123°–125°, soluble in water and alcohol, but insoluble in ether.

IV. Acids of the Cyclic (Chaulmoogric) Series: $C_nH_{2n-4}O_2$.

The acids belonging to this group are cyclic compounds and therefore contain only one pair of doubly-linked carbon atoms; hence they absorb only two atoms of halogen. The acids are also remarkable on account of their property of rotating the plane of polarised light.

Hydnocarpic acid, $C_{16}H_{28}O_2$, was isolated from the mixed fatty acids of hydnocarpus oil by crystallisation from alcohol. It is sparingly soluble in the usual organic solvents in the cold, with the exception of chloroform, in which the acid is easily soluble; $[\alpha]_D + 68{\cdot}1°$. On keeping, the acid becomes yellow, the melting-point, at the same time, being lowered; on distilling under diminished pressure, a brown resinous substance is left in the distilling flask.

Chaulmoogric acid, $C_{18}H_{32}O_2$, was prepared from the mixed fatty acids of chaulmoogra oil by crystallisation from petroleum spirit, subsequent distillation under diminished pressure and recrystallisation from alcohol. The crystals form colourless, glistening leaflets; $[\alpha]_D+62{\cdot}1°$.

V. ACIDS OF THE LINOLENIC SERIES: $C_nH_{2n-6}O_2$.

The acids of this series assimilate six atoms of hydrogen, or three molecules of iodochloride. They are therefore assumed to contain three pairs of doubly-linked carbon atoms. They readily absorb oxygen from the air, a property of which extensive use is made in the arts (*Drying oils*). According to Molinari, they absorb three molecules of ozone. By treatment with hydrogen in the presence of a catalyst, linolenic acid is converted into stearic acid.

Linolenic acid, $C_{18}H_{30}O_2$

$CH_3\,CH_2{\cdot}CH{:}CH{\cdot}CH_2\,CH{:}CH\,CH_2CH{:}CH[CH_2]_7CO_2H$

occurs in notable quantities in the drying oils, especially in linseed oil. According to Erdmann there exist two linolenic acids, α- and β-linolenic acid, of which the α-linolenic acid gives a crystalline hexabromide, melting at 179°. On reducing this crystalline hexabromide and again brominating the reduced linolenic acid, only 23 p.c. of the crystalline hexabromide is obtained, whence Erdmann and Bedford conclude that the reduced acid consists of a mixture of two, α- and β-linolenic acids. The isolation and determination of the crystalline hexabromide is made use of in the analytical examination of drying oils (*v. infra*).

Pure α-linolenic acid is a colourless liquid of sp.gr. 0·9046; on exposure to the atmosphere it absorbs oxygen rapidly and increases thereby in sp gr. The iodine value of the pure acid corresponds to that demanded by theory. On oxidising linolenic acid, a hexahydroxystearic acid (linusic acid), m.p. 203°–205°, is obtained.

*iso***Linolenic acid,** $C_{18}H_{30}O_2$. The existence of this acid was inferred by Hazura from the fact that he obtained on oxidising the mixed linseed oil acids with potassium permanganate an isomeride of linusic acid, termed *iso*linusic acid. This second hexahydroxy acid melts at 173°–175°. The existence of *iso*linolenic acid is doubtful (*see* LINSEED OIL).

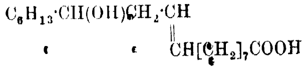
VI. ACIDS OF THE CLUPANODONIC SERIES: $C_nH_{2n-8}O_2$.

Clupanodonic acid, $C_{18}H_{28}O_2$, has been prepared from its octobromide by reduction with zinc and alcoholic hydrochloric acid. It is a pale yellow liquid having a fishy smell. The acid is characteristic of all fish, liver, and blubber oils. The most important derivative of this acid is the octobromide, the insolubility of which is utilised for the isolation of clupanodonic acid from a mixture of fatty acids and thus the recognition of fish, liver, and blubber oils (*v. infra*). The octobromide is insoluble in the usual organic solvents; it is only slightly soluble in hot benzene. It does not melt below 200°, but begins to blacken above this temperature.

VII. ACIDS OF THE RICINOLEIC SERIES: $C_nH_{2n-2}O_3$.

The acids belonging to this series are best characterised as 'oleic' acids in which one atom of hydrogen is replaced by a hydroxyl group. The most important representative of this series is:—

Ricinoleic acid, $C_{18}H_{36}O_3$



$$\begin{array}{l} C_6H_{13}{\cdot}CH(OH)CH_2{\cdot}CH \\ \qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\quad CH[CH_2]_7COOH \end{array}$$

discovered by Bussy and Lecanu in castor oil.

Pure ricinoleic acid is miscible with alcohol and ether in every proportion. The acid contains an asymmetric carbon atom; hence it is optically active: $[\alpha]_D+6{\cdot}25°$ to $+7{\cdot}5°$ (in acetone solution). On standing, the acid becomes spontaneously polymerised to form polyricinoleic acids, which are easily re-converted into ricinoleic acid by boiling with alcoholic potash and acidification of the soap. Ricinoleic acid assimilates two atoms of bromine or one molecule of iodochloride. The bromide is liquid. By hydrogen, in the presence of a catalyst, it is converted into hydroxystearic acid. The acid does not absorb oxygen on exposure to air. On treatment with ozone, it absorbs four atoms of oxygen, forming a perozonide.

By oxidation with an alkaline solution of potassium permanganate in the cold, two hydroxyl groups are assimilated with formation of trihydroxystearic acid. The statement by Hazura and Gruessner that two isomeric trihydroxystearic acids are formed and that consequently castor oil contains two isomeric acids, viz. ricinoleic and *iso*ricinoleic acids, is open to grave doubts (*see* Lewkowitsch, Chem. Techn. [i.]).

For the complicated reaction taking place on treating ricinoleic acid with concentrated sulphuric acid, *cp.* Lewkowitsch, *l.c.* On subjecting ricinoleic acid to dry distillation, optically active hydrocarbons are obtained.

Ricinelaidic acid is formed by treating ricinoleic acid with nitrous acid. It also is optically active; $[\alpha]_D+6{\cdot}670°$ (in absolute alcohol). The acid crystallises in needles, melting at 52°–53°.

VIII. DIHYDROXYLATED ACIDS: $C_nH_{2n}O_4$.

Dihydroxystearic acid, $C_{18}H_{36}O_4$. Only one dihydroxystearic acid has been found hitherto in a natural oil; it occurs to the extent of about 1 p.c. in castor oil. The acid is insoluble in ether, petroleum spirit, and benzene, slightly soluble in cold toluene, more so in the hot solvent; it dissolves in boiling alcohol and boiling acetic acid. Reducing agents readily convert it into stearic acid.

IX. DIBASIC ACIDS: ACIDS OF THE SERIES $C_nH_{2n-2}O_4$.

Three dibasic acids belonging to this series have been isolated from Japan wax by fractionating its insoluble mixed fatty acids *in vacuó*. The best known of the three acids is:—

Japanic acid, $C_{21}H_{40}O_4$, which appears to form, together with palmitic acid, a mixed glyceride. The acid crystallises from alcohol and chloroform in white laminæ; it is heavier than water; it dissolves very sparingly in water.

In addition to the above naturally occurring fatty acids, there are found in various products of the fat industries several hydroxylated acids or their inner anhydrides. These hydroxylated acids belong to the same series as the dihydroxylated, trihydroxylated, tetrahydroxylated, and hexahydroxylated acids obtained respectively from oleic, ricinoleic, linolic, and linolenic acids by oxidation with potassium permanganate in the cold. These acids are of great importance for the identification of the unsaturated fatty acids from which they have been derived.

A full description of these acids exceeds the limits of this article, all the more so as quantitative methods for their determination still require to be worked out. It must suffice, therefore, to refer to chapters III. and VIII. of Lewkowitsch's Chem. Techn., and to the following tables, detailing briefly the properties of the more important hydroxylated acids and of their acetylated products. The second table shows that the hydroxylated acids are best characterised by their notable acetyl values.

Acid	Formula	Melting-point °C	Solubility of the acid in					Obtained from
			Water		Alcohol		Ether	
			Cold	Hot	Cold	Hot		
α-Hydroxystearic	$C_{18}H_{35}O_2(OH)$	81-81·5	insoluble	insoluble	sparingly soluble	soluble	sparingly soluble	oleic; elaïdic acid
α-Hydroxystearic	$C_{18}H_{35}O_2(OH)$	77-79	insoluble	insoluble	sparingly soluble	less soluble than 1.10 acid	more soluble than 1.10 acid	'*iso*oleic' acid
Dihydroxystearic	$C_{18}H_{34}O_2(OH)_2$	137	insoluble	insoluble	sparingly soluble	soluble	sparingly soluble	ordinary oleic acid
Sativic . .	$C_{18}H_{32}O_2(OH)_4$	173	insoluble	sparingly soluble	sparingly soluble	soluble	insoluble	linolic acid
Linusic . .	$C_{18}H_{30}O_2(OH)_6$	203-205	sparingly soluble	soluble	sparingly soluble	sparingly soluble	insoluble	linolenic acid
*iso*Linusic .	$C_{18}H_{30}O_2(OH)_6$	173-175	sparingly soluble	readily soluble	soluble	soluble	insoluble	*iso*linolenic acid

Acid	Formula	Acetylated acid				Increase in weight on acetylating
		Formula	Molecular weight	Acetyl value	Saponification value	Per cent.
Hydroxystearic . . .	$C_{18}H_{35}O_2(OH)$	$C_{18}H_{35}O_2(O\cdot C_2H_3)O$	312	164·0	328·0	14·00
Dihydroxystearic . .	$C_{18}H_{34}O_2(OH)_2$	$C_{18}H_{34}O_2(O\cdot C_2H_3O)_2$	400	280·5	420·75	26·58
Trihydroxystearic . .	$C_{18}H_{33}O_2(OH)_3$	$C_{18}H_{33}O_2(O\cdot C_2H_3O)_3$	458	367·4	489·9	37·95
Tetrahydroxystearic (sativic)	$C_{18}H_{32}O_2(OH)_4$	$C_{18}H_{32}O_2(O\cdot C_2H_3O)_4$	516	434·8	543·6	48·27
Pentahydroxystearic . .	$C_{18}H_{21}O_2(OH)_5$	$C_{18}H_{31}O_2(O\cdot C_2H_3O)_5$	574	488·7	586·4	57·69
Hexahydroxystearic (linusic)	$C_{18}H_{30}O_2(OH)_6$	$C_{18}H_{30}O_2(O\cdot C_2H_3O)_6$	632	532·5	621·3	66·31

The methods applicable to the examination of fatty acids divide themselves naturally into (*a*) physical methods; (*b*) chemical methods.

(*a*) Physical Methods.

The physical methods, embracing the determination of the specific gravity, refractive index, rotatory power, and solubility, are applied in the same manner as described above for the glycerides.

More important than the determination of the solidifying and melting points of the glycerides is the determination of the solidifying point of the fatty acids, as valuable information of a discriminative nature can be obtained therefrom.

The *solidifying point of the fatty acids* forms the basis of the commercial valuation of such fats as tallow, bonefat, palm oil, and other vegetable fats. This number is known in commerce as 'titre test' and denotes the solidifying point taken under exactly determined conditions (*v. infra*).

The solidifying point is not a physical constant, inasmuch as it depends on the rate of cooling of a definite quantity examined under certain conditions; hence it is obvious that by varying these conditions, different results will be obtained. For commercial purposes, it is therefore most essential that a certain *modus operandi* be adhered to as strictly as possible. The mode of procedure proposed by Dalican has been adopted in this country, in the United States, and in France. This method has proved itself reliable in the author's own experience, extending over a great number of years. Fifty grams of the fat under examination are saponified, the separated fatty acids are freed from water and finally filtered through a dry plaited filter into a porcelain dish. The fatty acids are allowed to solidify and to stand overnight under a desiccator. (At the seventh International Congress, it was agreed that in those cases where rapidity in obtaining a result was of greater importance than strictest accuracy, the fatty acids may be allowed to stand for a few hours only.) The fatty substance is carefully melted in an air-bath or over a free flame, and as much of it is poured into a test-tube, 16 cms. long and 3·5 cms. wide, as will fill the tube more than half full. The tube is then fastened by means of a cork into a wide-mouthed bottle, 10 cms. wide and 13 cms high, and an accurate thermometer (graduated in tenths of degrees from about -5° to +60°, having a mercury bulb about 3 cms. long and 6 mm. in diameter, and carefully standardised with the aid of a 'normal thermometer'), is inserted in the fatty acids, so that the bulb is in the middle of the mass. When a few crystals appear at the bottom of the tube, the mass is stirred by giving the thermometer a rotatory movement, first three times from right to left, and then three times from left to right. The stirring is then continued, with a quick circular movement of the thermometer, without allowing it to touch the sides of the vessel, and taking care that all solidified portions, as they form, are well stirred into the mass until the latter has become cloudy throughout. The thermometer should now be observed carefully. A good plan is to write down the temperature at short intervals. At first the mercury will continue to fall, or at least remain stationary, then it will rise suddenly some tenths of a degree and reach a maximum, remaining stationary thereat for some little time before it falls again. This point is called the 'titre' or solidifying point of the mixed fatty acids. In the case of dark coloured fats, it may be impossible to observe the separation of crystalline matter. In such cases, it is best to make a preliminary experiment, which affords the necessary guidance.

TITRE TESTS OF MIXED FATTY ACIDS
(Lewkowitsch).

Class of oil	Kind of oil	Titre test °C.	Remarks
Drying oils	Linseed oil	20·6	
	Tung oil	37·2	
	Hemp seed oil	16·6	
	Safflower oil	16·0	
	Poppy seed oil	16·2	
	Soya bean oil	21·2	
Semi-drying oils	Cotton seed oil	32·0	Lowest
	,, ,,	35·2	Highest
	Maize oil	19·0	
	Sesamé oil	23·8	
	Croton oil	19·0	
	Curcas oil	28·6	
	Rape oil	13·6	
Non-drying oils	Peach kernel oil	13·5	
	Almond oil	11·8	
	Arachis oil	29·2	
	Koëme oil	38·8	
	Olive oil	17·2	Lowest
	,, ,,	26·4	Highest
	Ben oil	37·8	
Marine animal oils	Japanese sardine oil	28·2	
	Cod liver oil	13·9	Lowest
	,, ,,	24·3	Highest
	Seal oil	15·9	
	Whale oil	23·9	
Terrestrial animal oils	Sheep's foot oil	21·1	
	Horse's foot oil	28·6	
	Neat's foot oil	26·5	

Class of fat	Kind of fat	Titre test °C.	Remarks
Vegetable fats	Chaulmoogra oil	39·6	
	Pongam oil	44·4	
	Laurel oil	15·1	
	Carapa oil	34·9	
	Margosa oil	42·0	
	Niam fat	42·5	
	Mowrah seed oil	40·3	
	Shea butter	53·8	
	Palm oil, Bonny	35·9	
	,, ,, Bassam	38·47	
	,, ,, Lagos	43·925	
	,, ,, Old Calabar	44·60	
	,, ,, Salt Pond	44·475	
	,, ,, New Calabar	45·55	
	,, ,, Congo	45·05	
	Macassar oil	51·6	Lowest
	,, ,,	53·2	Highest
	Sawarri fat	47·0	
	Nutmeg butter	39·95	
	Cacao butter	48·3–49·6	
	Chinese vegetable tallow	45·2	Lowest
	,, ,, ,,	53·4	Highest
	Palm nut oil	20·5	Lowest
	,, ,,	25·5	Highest
	Coconut oil, commercial	22·55	Lowest
	,, ,, ,,	25·2	Highest
	,, ,, Cochin	25·2	
	Japan wax	59·4	

Class of fat	Kind of fat	Titre test °C.	Remarks
Animal fats	Horse fat	33·7	
	Horse marrow fat	38·55	
	Lard	42·0	
	Beef tallow, English	38·7	Lowest
	,, ,, ,,	45·1	Highest
	,, ,, N. American	41·1	Lowest
	,, ,, ,,	44·15	Highest
	,, ,, S. American	44·15	Lowest
	,, ,, ,,	46·25	Highest
	,, ,, Australian	38·3	Lowest
	,, ,, ,,	43·3	Highest
	Mutton tallow, English	41·5	Lowest
	,, ,, ,,	48·3	Highest
	,, ,, Australian	42·35	Lowest
	,, ,, ,,	48·05	Highest
	,, ,, N. Zealand	45·0	Lowest
	,, ,, ,,	48·0	Highest
	Beef marrow fat	38·0	

In Germany, Austria, and in the United States, slightly different methods of operating have been proposed (*see* Lewkowitsch, *loc. cit.*), but as Dalican's method has been made the basis of commercial transactions in this country, the United States, and France, new proposals for determining the 'titre,' however acceptable they may appear, have little chance of superseding the established method. The above table gives a list of titre tests collated from a very large number of observations made by the author.

(*b*) *Chemical Methods.*

The chemical methods are arranged here in a logical order, so that the order of the description may serve at the same time as a guide in the technical examination. (For other methods, which involve strictly scientific examination, *see* Lewkowitsch, vol. i. chap. xii.)

(1) Neutralisation Value—Mean Molecular Weight.

The neutralisation value indicates the number of milligrams of potassium hydroxide required to saturate one gram of the mixed fatty acids.

NEUTRALISATION VALUES OF FATTY ACIDS.

Acids	Formula	Molecular weight	Neutralisation value Mgrms KOH
Acetic . .	$C_2H_4O_2$	60	935·0
Butyric . .	$C_4H_8O_2$	88	637·5
Caproic . .	$C_6H_{12}O_2$	116	483·6
Caprylic . .	$C_8H_{16}O_2$	144	389·6
Capric . .	$C_{10}H_{20}O_2$	172	326·2
Lauric . .	$C_{12}H_{24}O_2$	200	280·5
Myristic . .	$C_{14}H_{28}O_2$	228	246·1
Palmitic . .	$C_{16}H_{32}O_2$	256	219·1
Stearic . .	$C_{18}H_{36}O_2$	284	197·5
Oleic . . .	$C_{18}H_{34}O_2$	282	198·9
Linolic . .	$C_{18}H_{32}O_2$	280	200·4
Hydnocarpic .	$C_{16}H_{28}O_2$	252	222·6
Chaulmoogric .	$C_{18}H_{32}O_2$	280	200·4
Linolenic . .	$C_{18}H_{30}O_2$	278	201·8
Clupanodonic .	$C_{18}H_{28}O_2$	276	203·2
Ricinoleic . .	$C_{18}H_{34}O_3$	298	188·3
Arachidic . .	$C_{20}H_{40}O_2$	312	179·8
Gadoleic . .	$C_{20}H_{38}O_2$	310	181·0
Erucic . .	$C_{22}H_{42}O_2$	338	166·0
Cerotic . .	$C_{26}H_{52}O_2$	396	141·7
Melissic . .	$C_{30}H_{60}O_2$	452	124·1
Hydroxystearic .	$C_{18}H_{36}O_3$	300	178·0
Dihydroxystearic	$C_{18}H_{36}O_4$	316	177·6
Trihydroxystearic	$C_{18}H_{36}O_5$	332	169·0
Sativic . .	$C_{18}H_{36}O_6$	348	161·2
Linusic . .	$C_{18}H_{36}O_8$	380	147·6

The determination of the neutralisation number is carried out in exactly the same manner as is described under the heading 'Acid Value.' As a rule, about 5 grams of the substance should be taken; smaller quantities should not be employed (if avoidable), as otherwise the errors of the method have too great an influence on the result. From the neutralisation number thus found, the mean molecular weight of the fatty acids may be calculated as follows: Let M be the molecular weight expressed in grams. Theory requires that M grams be neutralised by 56·1 grams of potassium hydroxide KOH. Let *n* be the number of grams of potassium hydroxide found by experiment to neutralise 1 gram of fatty acids; then we have the proportion

$$M : 56{\cdot}1 :: 1 : n\text{; hence, } M = 56{\cdot}1/n$$

n is found by multiplying the number found for 1 gram of fatty acid by 0·0561. If that number be *a*, we have

$$n = a \times 0{\cdot}0561$$

By substitution we obtain

$$M = \frac{56{\cdot}1}{a \times 0{\cdot}0561} = \frac{1000}{a}$$

The table in previous column contains the theoretical molecular weights and calculated[1] neutralisation values of pure fatty acids; they will serve as a guide to the proper interpretation of results obtained in the practical examination of mixed fatty acids.

(2) Lactones—Anhydrides.

If the fatty acids, instead of being titrated with aqueous alkali in the cold, were boiled with an excess of alcoholic potassium hydroxide solution (*see Saponification value*), the number of milligrams of potassium hydroxide thus required to saturate 1 gram of fatty acids should be the same as that found for the neutralisation value, provided the amount of unsaponifiable matter be negligible. In other words, the neutralisation and saponification values of fatty acids should be identical. In case, however, the fatty acids contain lactones, or anhydrides of the fatty acids, which do not combine with aqueous alkali in the *cold*, and are only hydrolysed on boiling with alcoholic potassium hydroxide solution, then the saponification value of the fatty acids will be higher than the neutralisation number.

The difference between saponification and neutralisation values furnishes a measure of the lactones or anhydrides present. The determination of lactones is of importance in the commercial examination of candle materials (*v.* Lewkowitsch, *loc. cit.*).

(3) Insoluble Fatty Acids (Hehner Value).

Three to four grams of fat are saponified as described under *Saponification value*, using, of course, double the amount of alcoholic potassium hydroxide solution stated there. The soap is dissolved in 100–150 c.c. of water (the alcohol is driven off completely until the soap has become pasty), acidified with dilute sulphuric acid and warmed until the liberated fatty acids float on the top as a clear oily layer. This is brought on to a filter-paper of about 4–5 inches diameter, previously dried at 100° and accurately weighed in a weighing bottle or a small beaker (covered with a watch-glass). The filter-paper should be of stout material, as ordinary filtering paper readily allows the liquid to run through turbid. A good plan to prevent this is to have the filter half full of hot water, before the fatty matter is transferred to it, and to keep it full until all the liquid is added. Finally, the fatty acids are washed on the filter with boiling water until a few c.c. of the wash-water do not redden sensitive tincture of litmus. In the case of fats belonging to the coconut oil or dika fat group, as also in the case of butter fat, 2000–3000 c.c. of wash-water are required. The washing being completed, the funnel with the filter is immersed in a vessel of cold water, so that the water outside and the acid inside are at the same level. The water is then allowed to drain off, the filter is transferred to the beaker in which it had previously been weighed, is dried at 100° for 2 hours, and weighed. The fatty matter is dried for another hour or an hour and a half, and weighed again. The difference between the two weights will, as a rule, be below 1 milligram.

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[1] For H=1; O=16; C=12.

Strictly concordant results are not obtainable by this method, as it entails a number of inherent errors, detailed consideration of which is required in each special case (see Lewkowitsch, Chem. Techn.).

Most oils and fats yield about 95 p.c. of insoluble fatty acids; only those fats which are characterised by high Reichert values yield less than 95 p.c. It should be noted that the 'fatty acids' include the unsaponifiable matter, unless the latter has been removed from the soap solution. In the majority of cases, and especially in analyses of unadulterated fats for commercial purposes, the amount of unsaponifiable matter may be neglected.

(4) Volatile Fatty Acids.

A notable amount of volatile fatty acids is indicated by a definite Reichert-Meissl value of the glycerides, as also by a notable titration number of the insoluble volatile fatty acids The approximate separation of the soluble volatile fatty acids has been described above (For further details and the application of the method for the determination of the volatile fatty acids in the examination of butter fat and mixtures thereof with coconut oil and palm-kernel oil, *see* Lewkowitsch, *loc. cit.*)

(5) Separation of Insoluble Saturated from Unsaturated Fatty Acids.

The presence of unsaturated fatty acids in the mixed insoluble fatty acids is detected in the readiest manner by determining the iodine value of the mixed fatty acids; this method offers an additional advantage in that it furnishes a measure of the unsaturated fatty acids, much as the iodine value of the oils and fats affords a measure of the unsaturated glycerides. The mixed fatty acids as obtained from the natural oils and fats will always have a definite iodine value.

The best—although still imperfect—method of separation is based on the solubility of the lead salts of the insoluble fatty acids in ether; in this menstruum the lead salts of the solid fatty acids, if free from liquid acids, are almost insoluble. This method is best carried out in the following manner as worked out in the author's laboratory; it consists of a combination of the several modifications of the original Gusserow-Varrentrapp method, proposed by Muter and de Koningh, and by Lane:—

3 to 4 grams of fatty acids are neutralised in a 300 c.c. flask with 50 c.c. of approximately half-normal aqueous potassium hydroxide solution. In case the original oil or fat be employed, 3-4 grams are saponified in the usual manner with 50 c.c. of approximately half-normal alcoholic potassium hydroxide solution in a 300 c.c. flask. Phenolphthalein is added, the solution is slightly acidified with acetic acid, and finally titrated with alcoholic potassium hydroxide solution until neutral. The solution is then diluted with water to about 100 c.c., 30 c.c. of a 10 p.c solution of lead acetate are diluted with 150 c.c. of water, heated to the boiling-point and gradually run into the soap solution, with constant shaking. The flask, containing the lead soap, is filled completely with hot water, and then allowed to cool. When the liquid has become clear it is poured off through a filter. As a rule, the solution is so clear that no solid particles will be found on the filter; should there be any, they must be brought back into the flask. The precipitate in the flask is washed thoroughly with boiling water, with the precaution of cooling the hot solutions before filtering, thus causing the lead salts to adhere to the sides of the flask. The last drops of water may be removed by means of a thin roll of filter-paper. It is not advisable to dry the lead salts, as in the case of drying oils they absorb oxygen from the air somewhat rapidly. Next, 150 c.c. of ether are added to the lead salts, and the flask is corked and shaken repeatedly, so that the salts may disintegrate. The flask is then attached to a reflux condenser and heated on a water-bath for some little time, with frequent shaking. The lead salts of the liquid fatty acids dissolve readily in the hot ether, conjointly with some fractions of the salts of the saturated acids; undissolved salts, if any, settle out at the bottom of the flask as a fine powder. If all operations are conducted somewhat rapidly and unnecessary exposure to the air is avoided, working in an atmosphere of an inert gas can be dispensed with. The ethereal solution is then allowed to cool down to the ordinary temperature and the solution filtered through a pleated filter (kept covered with a watch-glass) into a separating funnel. The insoluble salts are brought on to the filter by washing the flask three or four times with ether, 30 c.c. being used each time. The ethereal solution is then shaken with a mixture of one part of hydrochloric acid and four parts of water, in order to decompose the lead salts. The ether dissolves the free fatty acids as they are liberated, whilst the undissolved lead chloride settles out at the bottom of the separating funnel. After separation into two layers has taken place, the acid liquid is drawn off and the ethereal layer is washed with small quantities of water until the wash-water is free from acid. Finally, the ethereal solution is filtered through a small pleated filter into an ordinary flask. In case the liquid fatty acids consist chiefly of oleic acid, the results will be sufficiently accurate, if the ether be evaporated off on the water-bath and the residue dried in a water-oven. If, however, the presence of less saturated fatty acids (from linseed, soya bean, maize, marine animals oil) than oleic is suspected, the ethereal solution should be distilled off in a current of dry hydrogen or dry carbon dioxide. The flask is then immersed up to the neck in warm water, which is finally brought to the boiling-point. Thus the last traces of moisture are removed.

On the filter there remain the lead soaps of the saturated fatty acids, which are decomposed by treatment with hydrochloric acid, so that the saturated fatty acids can be removed and further examined. The determination of the iodine value of the liquid fatty acids will furnish an approximate indication of the composition of the liquid fatty acids.

(6) Separation and Estimation of Individual Saturated Fatty Acids.

In the present stage of our knowledge only the following solid acids can be determined with approximate accuracy.

Arachidic acid.—The solid fatty acids obtained from 10 grams of oil by the lead-salt-ether method are dissolved in 50 c.c. of 90 p.c. alcohol. In the presence of arachidic acid, a crystalline mass separates out from the cooled solution. This consists, in the case of arachis oil, of a mixture of arachidic and lignoceric acids. The crystals are filtered off and washed on the filter, first with a measured quantity of 90 p.c. alcohol, then of 70 p.c. (by volume) alcohol which dissolves but small quantities of the crude arachidic acid. The crystals are finally dissolved by pouring boiling absolute alcohol on the filter. The filtrate is received in a porcelain dish or in a flask, evaporated to dryness, and the residue is weighed. To the weight of crude arachidic acid thus found, the quantity dissolved by the 90 p.c. alcohol used for washing (taking as basis for calculation that 100 c.c. dissolve 0·0022 gram at 15°, or 0·045 gram at 20°) is added. Finally, the melting-point of the crude arachidic acid is determined. This should be from 71° to 72° (*cf.* Lewkowitsch, Chem. Techn.)

Stearic acid.—The determination of stearic acid is based on the principle used by Casamajor for the separation of sugars, and depends on the fact that on treating mixed fatty acids with an alcoholic solution of pure stearic acid saturated at 0°, all the lower saturated fatty acids, as also the unsaturated fatty acids, are dissolved, whereas stearic acid remains undissolved.

It should be noted that if any arachidic acid be present as well as stearic acid, the separated acid consists of a mixture of the two. In such cases it is advisable first to separate off the arachidic acid by the method described above.

This principle has been worked out by Hehner and Mitchell as a method which yields in many cases, but not in every case, reliable results (*cf.* Lewkowitsch, *loc. cit.*).

The stearic acid solution is prepared by dissolving about 3 grams of pure stearic acid in 1000 c.c. of warm (methylated) alcohol of sp.gr. 0·8183 (containing 94·4 p.c. of alcohol by volume) in a stoppered bottle. The bottle is immersed up to the neck in ice-water (kept in an ice-chest, well protected against radiation of heat), and allowed to stand in the ice-water overnight. After 12 hours, the mother liquor is siphoned off without removing the flask from the ice-water, by means of a small thistle funnel immersed in the alcoholic solution and covered with a piece of fine calico (so as to retain the separated stearic acid crystals in the flask). The funnel is twice bent at right angles, and is best fitted into a suction bottle, so that the clear liquor can be drawn off by means of a filter-pump. The method is carried out as follows: 0·5 gram to 1 gram of the mixed fatty acids, if solid, or 5 grams if liquid, are weighed accurately in a flask and dissolved in 100 c.c. of the above alcoholic stearic acid solution. The flask is placed in ice-water overnight, the mixture is agitated the following morning while the flask is still kept in the ice-water, and then allowed to stand for at least half an hour in the ice-water in order to promote crystallisation. The alcoholic solution is then filtered off as described above, care being taken to draw off the solution as completely as possible. The residue in the flask is washed three times in succession with 10 c.c. of the alcoholic stearic acid solution, previously cooled down to 0°. The crystals adhering to the calico of the thistle funnel are then washed with hot alcohol into the flask, the alcohol is evaporated off, the residue dried at 100° and weighed. In case the melting-point be much below 68·5°, the author considers it necessary to treat the residue once more as described above. A correction of 0·005 gram should be made for the stearic acid retained on the walls of the flask and in the adhering stearic acid solution.

It has been shown by Holland, Reed, and Buckley that a source of error in this method is the occasional supersaturation of the solution owing to the presence of insufficient stearic acid. To obviate this they add a weighed quantity of pure stearic acids to the fatty acids, and deduct this from the weight of the deposit.

(7) Detection, Separation, and Approximate Estimation of Individual Liquid Fatty Acids—Oleic, Linolic, Linolenic, Clupanodonic.

The liquid fatty acids are separated from the total mixed fatty acids by the lead-salt-ether method; thus preliminary information is obtained as to which fatty acids may be present. In the present state of our knowledge, attention can only be directed to the detection and determination of oleic, linolic, linolenic, and clupanodonic acids. If the iodine value be found to lie in the neighbourhood of 90, the liquid fatty acids may be considered as consisting of practically pure oleic acid. If the iodine value be much higher than in the case of the majority of pure vegetable oils, the presence of linolic and linolenic acids must be suspected; in the case of oils, belonging to the marine animal oils, the presence of clupanodonic acid must be expected: in the case of mixtures, of course, the presence of all these acids has to be assumed.

The presence of linolenic and (or) clupanodonic acids is ascertained by the bromide test, which permits at the same time of a quantitative determination of the insoluble bromides. The bromination test can be applied to the original mixed fatty acids without the necessity of separating the solid from the liquid acids. The mixed fatty acids are brominated in the same manner as already described in the bromide test: 0·3 grams of the fatty acids are dissolved in glacial acetic acid, and the solution is cooled in a corked flask to 5°. The further treatment is identical with that described above (*Bromide test*). The ether-insoluble bromo derivatives consist either of octobromide or of hexabromide, or of a mixture of both. If the melting-point of the insoluble bromides lies between 175°–180°, linolenic hexabromide derived from a drying oil has been obtained. If the bromide has not melted at 180° or not completely melted, and blackens on heating to 200° or above, then an octobromide, characteristic of a marine animal oil, is present.

If a mixture of hexabromides and octobromides be suspected, the bromides are separated by boiling with benzene, in which the octobromides are insoluble (*cp.* Lewkowitsch, *loc. cit.*). Researches (unpublished), made by the author, prove that it is not permissible to calculate the amount of hexabromides to drying oil, as not only a certain amount of hexabromides remains dissolved, but also because liquid isomerides of hexabromides appear to be formed.

The filtrate from the octobromides and (or) hexabromides contains, in addition to some dissolved hexabromides, tetrabromides and dibromides, the former can be isolated by evaporating off the ether and treating the residue with boiling light petroleum. On cooling, crystals separate out which represent, in most cases, a mixture of hexabromides and tetrabromides and exhibit melting-points lying between 170° and 136°. Thus the author found in the separated fatty acids of linseed oil, 39·37 p.c. of hexabromides of m.p. 181°, 3·09 p.c. of bromides, m.p. 151°, 7·83 p.c. of bromides, m.p. 142°, and 2·38 p.c. of bromides, m.p. 135°–136°. By repeating the treatment with ether and by renewed re-crystallisation from boiling petroleum spirit, tetrabromides of the approximately correct melting-point of pure crystalline linolic tetrabromide, viz. 114°, can be obtained.

The following table contains the amounts of insoluble bromides found in the mixed fatty acids from vegetable oils and marine animal oils.

—	Kind of oil	Yield of ether-insoluble bromide from fatty acids per cent
Hexabromides	Linseed (iodine value 181)	29·06 ; 29·34
	,, (,, ,, 184)	31·31 ; 30·41 ; 30·80
	,, ,, ,, 190·4)	38·1 ; 42·0
	,, liquid acids (iodine value 208)	34·9
	Candle nut	11·53 ; 11·23 ; 12·63
	Stillingia	25·78
	Safflower	1·65 ; 0·65
	Soya bean	5·1
	Rape	2·4 ; 3·4
Octobromides	Japan fish (old sample)	23·04 ; 23·32
	,, (fresh samples)	44·2 ; 47·1
	Deodorised fish	38·42 ; 39·2
	Cod liver, Norwegian	29·86 ; 30·36
	Newfoundland cod	39·1 ; 37·76
	Shark liver	12·68 ; 15·08
	Seal	19·53 ; 19·93
	Whale (old sample)	12·38 ; 12·44
	,, (fresh samples)	22·59 ; 27·77
	Herring	12·7 ; 21·7

In the case of semi-drying oils, which are practically free from linolenic acid and contain considerable amounts of linolic acid, the bromination may be carried out in petroleum spirit, when linolic tetrabromide of the melting-point 112°–113° can readily be obtained. In this case also, isomeric, soluble bromides are formed, especially if an excess of bromide had been used, so that the weight of the tetrabromides is much (by 50 p.c.) below the actual amount of linolic acid present. The following tables contain a number of determinations carried out in the author's laboratory.

Oil		Linolic acid calculated from separated tetrabromide	
Soya bean oil	. .	21	p.c.
Maize oil	. . .	28	,,
Cotton seed oil	. .	21–24	,,
Sesame oil	. . .	15·6–16·4	,,

(8) Estimation of Oxidised Fatty Acids.

Under the term 'oxidised' acids is comprised a class of fatty acids occurring in those oils and fats which have been treated with oxidising agents, as in the process of blowing with air or oxygen. The change which some of the unsaturated acids undergo is not yet fully understood, but this much is certain, that through 'blowing' or 'oxidising' a certain proportion of acids is obtained which are characterised by their insolubility in petroleum spirit.

The quantitative estimation of oxidised acids is carried out by Fahrion's method as follows: 4 to 5 grams of the sample are saponified in the usual manner with alcoholic potassium hydroxide solution; the alcohol is evaporated off, the soap is dissolved in hot water, transferred to a separating funnel, and decomposed with hydrochloric acid. After cooling, the liquid is shaken with petroleum spirit (boiling below 80°) and allowed to stand until it has separated completely into two clear layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or form a sediment in the petroleum layer. The aqueous layer is drawn off, the petroleum layer poured off, if necessary through a filter, and the oxidised acids are washed with petroleum spirit to remove adhering ordinary fatty acids. In case the amount of oxidised fatty acids be large, it is advisable to dissolve them in alkali, decompose the soap with hydrochloric acid, and shake out again with petroleum spirit, so as to remove completely any occluded soluble fatty acids. The oxidised acids are then dissolved in warm alcohol or ether, the alcoholic or ethereal solution is transferred to a tared basin, the alcohol or ether is evaporated off, and the residue dried until the weight remains constant. Thus the proportion of oxidised acids is found. (For further information, *cp.* Lewkowitsch, *loc. cit.*)

III. Examination of the Unsaponifiable Matter.

The unsaponifiable matter is isolated in substances as described above and can be immediately further examined. In case a sample under examination has not been adulterated with mineral oil, rosin oil, or tar oil, the amount of unsaponifiable matter will, as a rule, be very small. As stated already, the unsaponifiable matter consists chiefly of sterols; in the case of vegetable oils of *phytosterol* (mostly *sitosterol*); and in the case of animal oils and fats of *cholesterol.*

In addition to sitosterol, there has also been found in a number of vegetable oils, *stigmasterol*; and in rape oil, *brassicasterol*. The last two phytosterols cannot be considered here (*cp.*, however, Lewkowitsch, *loc. cit.*).

The examination of the unsaponifiable matter furnishes, therefore, a means of distinguishing between vegetable and animal oils and fats. In case a mixture of both vegetable and animal products be present, a mixture of phytosterol and cholesterol is, of course, obtained.

For the examination of the unsaponifiable matter, the isolated substance is dissolved in the smallest possible amount of absolute alcohol and allowed to crystallise. If notable amounts of colouring matters and resinous substances are absent, as a rule well-defined crystals are obtained. Otherwise, the unsaponifiable matter must be dissolved in 95 p.c. alcohol and the solution decolorised by animal charcoal. The crystals should then be examined under the microscope. Cholesterol crystallises in the forms shown in Fig. 5, sitosterol in crystals shown in Fig. 6.

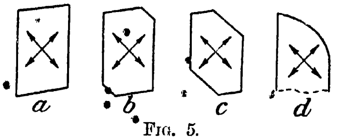

FIG. 5.

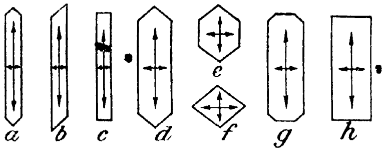

FIG. 6.

In the presence of both cholesterol and sitosterol, the microscopic examination furnishes very uncertain results (*cp.* Lewkowitsch, *loc. cit.*).

The uncertainty inherent in the microscopic test is removed by carrying out Bomer's phytosteryl acetate test.

Phytosteryl acetate test.—The alcoholic solution containing the crystals is evaporated to dryness on a water-bath, and the residue heated for 2 or 3 minutes in a small porcelain dish with acetic anhydride (2 to 3 c.c. per 100 grams of original oil or fat) over a small flame until the solution boils, the dish being covered with a watch-glass. The watch-glass is then removed, and the excess of acetic anhydride evaporated off on the water-bath. The contents of the dish are next heated with the smallest possible quantity of absolute alcohol; in order to prevent immediate solidification or crystallisation, a few c.c. of alcohol are added, when the mass is allowed to crystallise. By spontaneous evaporation, about one-half or one-third of the alcohol volatilises and the acetates crystallise out. The crystals are filtered off through a small filter, and washed with a little 95 c.c. alcohol. The acetates are brought back from the filter into the dish, dissolved in 5 to 10 c.c. of absolute alcohol, and again allowed to crystallise. The crystals are filtered off, and their melting-point is determined. Since cholesteryl acetate melts at 114·3°–114·8° (corr.), whereas crystals of sitosteryl acetate obtained from different oils and fats melt above 125°, the melting-point of the second crop of crystals will furnish *preliminary* information as to whether cholesterol only, or sitosterol only is present. Ultimate reliance should not, however, be placed on the melting-point of the second crop of crystals, for in most cases it is necessary to recrystallise the crystals at least three more times. If the melting-point of the fifth (or seventh) crop of crystals be found to lie below 115° or 116°, the absence of sitosterol may be regarded as certain. A gradual and distinct rise of the melting-points, above 114°, in the successive crops of crystals, is the best indication as to the procedure to be adopted.

A rapid method of separating cholesterol and phytosterol, devised by Windaus, is to treat the mixed fatty acids with digitonin, which precipitates characteristic digitonides of the alcohols. In a simple modification of this test the 50 grms. of the melted fat are stirred for 5 minutes at 60°–70° with 20 c.c. of a 1 p.c. alcoholic solution of digitonin, and the precipitate filtered off and converted into phytosteryl or cholesteryl acetate.

The cholesteryl acetate test is absolutely reliable, and superior to all other tests aiming at the detection of vegetable oils and fats in animal oils, such as the detection of coconut oil in butter fat or of vegetable fats and oils in lard. The sensitiveness of this test is so great that even 1 p.c. of an added vegetable oil or fat can be detected. This great sensitiveness has led to endeavours to circumvent and render illusory the indications of the phytosteryl acetate test by adding to fats adulterated with vegetable oils or fats, minute quantities of paraffin wax. For the determination of such added paraffin wax and the removal thereof, *see* Lewkowitsch, *loc. cit.*

If large quantities of unsaponifiable substances have been mixed with an oil or fat—which is readily ascertained in the saponification test by obtaining an abnormally low saponification value—then fraudulent admixture with solid or liquid hydrocarbons may be considered as established. Solid hydrocarbons are recognised by their consistence and identified by their melting-points. Liquid unsaponifiable substances consist of hydrocarbons, belonging to one of the following three groups:—

(*a*) mineral oils, (*b*) rosin oils, (*c*) tar oils.

For the identification and approximate determination of these, *see* Lewkowitsch, Chem. Techn.

The foregoing methods should enable the analyst to identify the more common individual oils and fats and recognise them when mixed, and to determine approximately their relative proportion, but it must be borne in mind that the introduction of hydrogenated oils (*q.v.*) as commercial products has greatly increased the difficulty of the problem. In order to facilitate the problem, the following tables, arranged in the order of a practically natural system, should be consulted. For a number of examples which may be of assistance in the examination of complicated mixtures, and for particulars of less known fats, *cp.* Lewkowitsch, *loc. cit.*

VEGETABLE

			Characteristics							
		Oils	Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value	Reichert (R.) or Reichert-Meissl (R.-M.) value	Insoluble fatty acids + unsaponifiable matter
			°C.		°C.	°C.	KOH mg	Per cent.	1/10 N.-KOH c.c.	Per cent.
Drying oils		Perilla	20·0	0·9306	—	—	189·6	206	—	—
		Linseed	15·0	0·9315–0·9345	−27	−20	192–195	171–201	—	95·5
		Tung (a) Chinese	15·0	0·9360–0·9432	below −17	—	193·0	150–165	—	92·2
		(b) Japanese								
		Candlenut	15·5	0·9256	—	liquid at −18	192·6	163·7	—	95·5
		Hempseed	15·0	0·9255–0·9280	−27	—	192·5	148·0	—	—
		Walnut; Nut	15·0	0·9250–0·9260	−27·5	—	195·0	145·0	—	95·4
		Safflower	15·5	0·9251–0·9280	—	—	186·6–193·3	129·8–149·9	·154 (R.-M.)	95·37
		Poppy seed	15·0	0·9240–0·9270	−18·0	—	195·0	133–143	0	95·2
		Sunflower	15·0	0·9240–0·9258	−18·5	—	193·5	119–135	—	95·0
		Soya bean	15·0	0·9242–0·9270	−8·0	—	192·7	137–141	—	95·5
Semi-drying oils		Cameline (German Sesamé)	15·0	0·9200–0·9260	−18·0	—	188·0	135–142	—	—
	Cotton seed oil group	Pumpkin seed	15·0	0·9237	−15·5	—	188·4	123–130	—	96·2
		Maize; corn	15·5	0·9213–0·9255	−10 to −20	—	188–193	113–125	4–5 (R.-M.)	93–96
		Madia	15·0	0·9285	−12·0	—	192·8	117–119	—	—
		Beech nut	15·0	0·9206–0·9225	−17·0	—	191–196	104–111	—	95·2
		Kapok	18·0	0·9199	—	—	181·0	116·0	—	94·9
		Cotton seed	15·0	0·9220–0·9250		3 to 4	193–195	108–110	—	95–96
		Sesamé	15·0	0·9230–0·9237	−5·0	—	189–193	103–108	1·2 (R.-M.)	95·7
		Curcas, purging nut	15·5	0·9204	−8·0	—	193·2	98–110	0·5 (R.-M.)	95·3
		Brazil nut	15·0	0·9180	0·4		193·4	90–106	—	—
		Croton	15·0	0·9500	−16·0		210–215	102–104	12–13·6 (R.-M.)	89·0
	Rape oil group	Ravison	15·5	0·9183–0·9217	−8·0	—	174–179	101–122	—	—
		Hedge mustard	15·0	0·9175	−8·0	—	174	105	—	—
		Rape (Colza)	15·5	0·9132–0·9168	2 to −10		170–179	94–102	0·3	95·1
		Black mustard	15·0	0·916–0·920	−17		174	96–110	—	95·1
		White mustard	15·5	0·914–0·916	−8 to −16	—	170–174	92–97	—	96·2
		Radish seed	15·0	0·9175	−10 to −17·5		173–178	93–96	0·33 (R.-M.)	95·9
		Jamba	15·0	0·9154	−10 to −12	—	172·3	95·4	—	—
Non-drying oils	Almond oil group	Cherry kernel	15·0	0·9234	−19 to −20	—	193–195	110–114	—	—
		Apricot kernel	15·5	0·9195	−14	—	192·5	96–108	0	95·4
		Plum kernel	15·0	0·9160–0·9195	−5 to −6	—	191·5	93·3–100·3	—	—
		Peach kernel	15·0	0·918–0·9215	below −20		192·5	93–109	—	—
		Almond	15·0	0·9175–0·9195	−10 to −20	—	191	93–97	—	96·2
		Arachis (ground nut)	15·0	0·9170–0·9209	−3 to 0	—	190–196	83–100	—	95·8
	Olive oil group	Hazel nut	15·0	0·9146–0·9170	−17	—	192	83–90	0·99 (R.-M.)	95·6
		Tea seed	15·0	0·9163–0·927	−5 to −12		189–195	88–92·7	—	91·5
		Olive	15·0	0·916–0·918	−6 to 2	—	185–196	79–88	0·3	95·0
		Olive kernel	15·0	0·9184–0·9191	—	—	183	87·4	—	—
		Ben	15·0	0·9120–0·9198	0		—	82·0	—	—
	Castor oil group	Grape seed	15·0	0·935	−10 to −13	—	178·5	96·6	0·46 (R.-M.)	92·13
		Castor	15·5	0·9600–0·9679	−10 to −18	—	183–186	83–86	1·4	—

OILS.

Refraction			Variables		Characteristics of fatty acids									
Butyro-refractometer		Acetyl value	Acetyl value	Acid value	Specific gravity		Solidifying point		Melting-point	Neutralisation value	Iodine value		Refraction	
°C.	Scale division			KOH mg	°C.		°C.	Titre °C	°C	KOH mg	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	—	—	—	—	—		- 5	197	210 0	—	—	—
20	84-90	—	3·98	0·8-8 4	15 5	0 9233	13-17	19 4	17 21	197	179 182	190 201	60	1·4546
40	72·5	—						20 6						
—	—	—	—	7 6 12	—	—	31-34	37 2	31 ; 43 8	188 8	144 159	—	—	—
15	76 0	—	9·86	8 1	—	—	15 0	—	20 21	—	—	—	—	—
—	—	—	—		—	—	15 0	16 6	18 19	—	111 0	—	—	—
40	64 8	—	—	—	—	—	16 0	—	16 18	—	150 0	167	—	—
40	65·2	—	[illegible]	0 33 20		—	—	—	—	—	—	—	—	—
40	63 4	—	—	0 7-11	100	0·8886	16 5	16 2	20 5	199	139 0	150	60	1·4506
25	72 2	—	—	11 2	—	—	18 0	—	22 21	201 6	124-134	154 3	60	1·4531
—	—	—	—	1 5	—	—	24 0		28 0	—	119 0	—	—	—
—	—	—	—	—	—	—	11-13	—	18 20	—	136 8	-165·4	—	—
25	70 2-72 5	—	—	—			21 5	—	28-29	197	—	—	—	—
—	—		7 5-8 75	1 7-20 6		—	16 11		18 20	198 4	119 5	140-144	—	—
—	—	—	—	—	—	—	20 22	—	23-26	—	120 7	—	—	—
—	—	—	—	—	—	—	17 0	—	23-24	—	111·0	—	—	—
—	—	—	—	—	—	0 9162	24-23	—	29 0	191	108 0	—	—	—
25	67·6-69 4	—	7 6-18	0	15 5	0 9206-0 9219	32-35	32 35	35 38	202-208	111 115	147-151	60	1·4460
25	68·0	—	—	0 23 66 (!)	—	—	23 5	22 9-23 8	26 32	200 4	110 45	129-136	69	1·4461
25	65 0		7 5	0 7-8 5	—		26 5	28	27 5-30·5	—	105·1	—	—	—
40	56 5						25 7							
—	—	—	—	—	—	—	31 1	—	28 30	—	108 0	—	—	—
27	77 5	—	19 32	—	—		16 7	19	—	201	111 5	—	—	—
20	73 74	—	—	1 8-12	100	0 8802	—	—	—	—	—	124 2	—	—
25	70 5 71·5	—	—	—	—	—	—	—	—	—	—	—	—	—
25	68 0	—	14 7	1 4-13 2	100	0 8758	16 0	12 13	16-19	185	99-103	121-125	60	1·4091
40	59·5	—	—	1 36-7·35	—	—	15 5	—	16 0	—	109 6	—	—	—
40	58 5	—	—	5 4	—	—	—	—	15-16	—	95 3	—	—	—
40	57·5	—	—	14·5	—	—	15 13	—	20 0	—	97 1	—	—	—
—	—	—	—	—	—	—	16-11	—	19-21	173·0	96·1	—	—	—
—	—	—	—	—	—	—	15-13	—	19 21	189	109 0	124·7	—	—
25	66·6	—	—	0·64	—	—	0	—	3·4	194	103·0	111·5	—	—
—	—	—	—	0 55	—	—	15-13	—	20-22 3·5	200 5	103(!)	98 6	—	—
25	66 1-67·2	—	—	—	—	—	—	13-13 5	10 18	200·9	94-101	101·9	—	—
25	64·4	—	—	—	—	—	5 0	19 1-11 8	13-14	204	93-96·5	101 7	60	1·4461
25	66-67·5	—	—	1·5	100	0·8790	26 0	29 2	27 7-32	201·6	96-103	105-128	60	1·4461
—	—	—	3·2	—	—	—	19-20	—	22-24	200·6	90·3	91·3-97·6	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
25	62·4	—	10·64	1·9-50	100	0 8749	22-17	17 2-26 4	24-27	193	86-90	93·5-103·5	60	1·4410
—	—	—	—	2 3·5	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	16·2	—	—	20-18	—	24·0	187·4	99·0	—	—	—
25	78	146·7-150	—	0·14-54 61	15·5	0·9509	3·0	—	13·0	192·1	87-93	106·9	60	1·4546

VEGETABLE

	Fat	Characteristics							
		Specific gravity		Solidifying point	Melting-point	Saponification value	Iodine value	Reichert (R.) or Reichert-Meissl (R.-M.) value	Insoluble fatty acids + unsaponifiable matter
		°C.		°C.	°C.	KOH mg.	Per cent.	$\frac{1}{10}$N.-KOH c.c.	Per cent.
Laurel oil group[1]									
	Laurel	15·0	0·9332	25·0	32-34	197·9	68-80	1·6	—
Palm oil group	Mowrahseed Mahua butters	15·0	0·9175	36·0	42·0	188-192	50-62	—	94·76
	Mowrah butter Illipé butter	100·0 (100=1)	0·8981	19-22	28-31	190-194	53-67	0·5-0·9 (R.-M.)	94·82
	Macassar oil Kusum oil	15·0	0·9240	10·0	22·0	221·5	48·55	—	91·5
	Palm oil	15·0	0·921-0·9245	—	27-42·5	196-202	51·5	0·5	94·97
	Phulwara butter	100·0	0·8970	—	39·0	190·8	42·1	0·44	94·86
Myristica group									
	Mace butter (Nutmeg butter)	15·0	0·945-0·996	41-42	38-51	154-191	40-52 (50-81)	1-4·2 (R.-M.)	—
Cacao butter group	Shea butter (Galam butter)	15·0	0·9175	17-18	25·3	179-192	56·6	—	94·76
	Mkanyi fat	15·0	0·9298	38·0	40-41	190·5	41·9	1·21 (R.-M.)	95·65
	Malabar tallow	15·0	0·9150	30·5	36·5	188·7-192	38·2	—	0·2-0·44 (R.-M.)
	Cacao butter	15·0	0·9500-0·976	23-21·5	28-33	193·55	32-41	0·2-0·8 (R.-M.)	94·59
	Chinese vegetable tallow	15·0	0·9180	27-31	36-46	200-3	28-37	—	—
	Kokum butter (Goa butter)	40·0 (15=1)	0·8952	37·6-37·9	41-42	187-191	33·6	0·1-1·5 (R.-M.)	95·1
	Borneo tallow	—	—	—	35-42	—	(31 ?)	—	—
Coconut oil group	Mocaya oil	—	—	22·0	24-29	240·6	24·63	7·0 (R.-M.)	—
	Maripa fat	100·0 (15·5=1)	0·8686	24-25	26·5-27·0	270·5	17·35	4·45 (R.-M.)	88·88
	Palm kernel oil Palm nut oil	15·5 (15·5=1)	0·9520	20·5	23-28	242-250	13-14	5-6 (R.-M.)	17·6-91·1
	Coconut oil	40·0 (15·5=1)	0·9115	22-14	21-24	246-260	8-9·5	7-8·4 (R.-M.)	88·6-90
Dika fat group	Dika oil (oba oil, wild mango oil)	—	0·8200	34·8	41·6	—	31·1	—	—
	Japan wax	15·0	0·9700-0·980	48·5-53	50-54	217-237·5	4·9-8·5	—	90·6
	Myrtle wax	15·0	0·995	39-43	40-44	208·7	10·7	—	—

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[1] *Cp.* Lewkowitsch, Bulletin Société Chimique de

FATS.

Refraction		Variables		Characteristics of fatty acids									
Butyro-refractometer		Acetyl value	Acid value	Specific gravity		Solidifying point		Melting-point	Neutralisation value	Iodine value		Refraction	
°C.	Scale divisions		KOH mg	°C.		°C.	Titre °C.	°C.	KOH mg	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	26 3	—	—	—	15 1	—	—	81·8	—	—	—
—	—	—	34·56	—	—	38-40	40·3	45 0	—	56·6	—	—	—
40	521	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	6 2–35·4	—	—	—	51·6-53·2	52 55	191·6	50–58	103·2	—	—
—	—	18·0	24–200	100 0	0 8701	—	35 9–45 5	47–50	205·6	53·3	94·6	—	—
40	48·2	—	—	—	—	—	—	—	—	—	—	—	—
40	48–85	—	17–44·8	—	—	40 0	42 5	42 5	—	—	—	—	—
—	—	—	29·4	—	—	38·0	53 8	58·0	—	56-57·2	—	—	—
—	—	—	23 3	—	—	57·5	61·5	59–61·5	—	42 1	—	—	—
—	—	—	38 0	—	-	54 8	—	56 6	—	—	—	—	—
40	46–47·8	2·[illegible]	1 1–1·88	—	—	47–45	48 3	48–50	190 0	33–39	—	60	1·422
—	—	—	2 2–7·5	—	—	—	45 2–53·5	53–57	182–208	30-39	—	—	—
25	1·4628	—	21·0	—	—	59·4	—	60–61	198 9	—	—	—	—
—	—	—	20·0	—	—	53·5–54	—	—	—	—	—	—	—
—	—	—	—	—	—	22–20	—	23–25	254·0	—	—	—	—
—	—	—	—	100·0 (15·5=1)	0·8230	25·0	—	27·5–28·5	—	12·15	—	—	—
40	36·5	1·9–8·4	8·36	—	—	—	20·5–25·5	25–28 5	258–264	12·0	—	60	1·4310
40	+34	0·9-12·3	5–50	98-99 (15·5=1)	0·8354	20–16	22·5–25·2	25–27	258-266	8·4–9·3	18·6	60	[illegible]
—	—	—	19·6	—	—	—	—	—	—	—	—	—	—
—	—	27–[illegible]1·2	7·33	98–99 (15·5=1)	0·8480	53·0–56·5	59·4	56–62	213·7	—	—	—	—
—	—	—	3–4·4	—	—	46·0	—	47·5	230·9	—	—	—	—

France 1909 (Conférence : Les Corps Gras), XLII.

ANIMAL

	Oils	Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value	Reichert (R.) or Reichert-Meissl (R.-M.) value	Insoluble fatty acids + unsaponifiable matter
		°C.		°C.	°C.	KOH mg.	Per cent.	$\frac{1}{10}$N.-KOH c.c.	Per cent.
Fish oils	Menhaden	15·5	0·927–0·933	−4	—	190·6	139–173	1·2	—
	Sardine	15	0·9330	—	—	—	161–193	—	94·5
	Japanese Sardine	15	0·9160	—	20–22	189·8–192·1	100–164	—	96–97
	Salmon	15·5	0·9258	—	—	182·8	161·4	0·55	95·02
	Herring	15·5	0·9202–0·939	—		171–194	123·5–142	—	95·64
	Stickleback	—	—	—	-	—	162·0	—	95·78
	Sturgeon	15	0·9236	—	- -	186·3	125·3	—	—
	Sprat	15·5	0·9284	—	- -	—	—	—	—
Liver oils	Cod liver	15	0·9210–0·9270	0 to −10	- -	171·0–189	167	—	95·3
	Skate liver	15	0·9307	—	—	185·4	157·3	—	94·7
	Tunny liver	—	—	—	—	—	155·9	—	95·79
	Shark (arctic)	15	0·9163	—	—	161·0	114·6	- -	86·9
	Coal fish	15	0·925	—	—	177–181	137–162	—	—
	Hake liver	15·5	0·9270	—	—	—	—	—	—
	Ray liver	15·5	0·9280	—	—	—	—	—	—
	Ling liver	15	0·9200	—	—	184·1	132·6	—	—
Blubber oils	Seal	15	0·9155–0·9263	−2 to −3	-	189–196	127–141	0·07–0·22	95·45
	Whale	15·5	0·9250	under −2		188·0	121–130	0·7–2·04	93·5
	Dolphin black fish Body oil	15	0·9180	under −3	—	197·3	99·5	5·6	93·07
	Jaw oil	—	—	—	- -	290	32·8	65·92	66·28
	Porpoise, Body oil	15	0·9258	−16	---	195	—	23·5	—
	,, Jaw oil	15	0·9258	—	—	254–272	22–50	47·77–65·8	70·23
Non-drying oils	Sheep's foot	15	0·9175	0–15	—	194·7	74·2	—	—
	Horse's foot	15	0·913–0·927	—	—	195·9	73·8–90	—	—
	Neat's foot	15	0·914–0·916	0–15	—	194·3	69·3–70·4	—	—
	Egg	15	0·9144	8–10	22–25	184·4–190·2	68·5–81·6	0·40–0·7 (R.-M.)	95·16

ANIMA

	Fat	Specific gravity		Solidifying point	Melting point	Saponification value	Iodine value.	Reichert (R.) or Reichert-Meissl (R.M.) value	Insoluble fatty acids + unsaponifiable matter	Refraction Butyro-refractometer	
		°C.		°C.	°C.	KOH mg.	Per cent.	$\frac{1}{10}$N—KOH c.c.	Per cent.	°C.	Scale division
Drying fats	Ice bear	15	0·9256	—	—	187·9	147·0	—	—	—	—
	Rattlesnake	15	0·9217	—	—	210·9	105·6	—	—	—	-
Semi-drying fats	Blackcock	15	0·9296	—	—	201·6	121·1	2·1	—	—	—
	Hare	15	0·9349	17–23	35–40	200·9	102·2	1·59	95·4	40	49·0
	Rabbit, wild	15	0·9393	17–22	35–38	199·3	99·8	0·7	—	—	—
	Rabbit, tame	15	0·9342	22–24	40–42	202·6	67·6	2·8	95·5	40	49·0
	Wild duck	—	—	15–20	—	198·5	84·6	1·3	—	—	—
	Domestic duck	—	—	22–24	36–39	—	58·5	—	—	—	—
	Horses' fat	15	0·9189	43–30	34–54	195–197	71–86	0·2–0·4	95–96	40	53·7
Non-drying fats	Horse marrow fat	15	0·9204–0·9221	24–20	35–39	199·8	79·1	1·0	—	—	—
	Domestic goose	15	0·9274	18–20	32–34	193·1	67–71	0·98	95·0	40	50–50·
	Wild goose	15	0·9158	18–20	—	196·0	99·6	0·2–0·3 (R.-M.)	—	—	—
	Lard: Hog, domestic	15	0·934–0·938	27·1–29·9	36–40·5	195·4	50–70	—	93–96	40	48·6–51·2
	Lard: Hog, wild	15	0·9424	22–23	40–44	195·1	76·6	0·68	—	—	—
	Beef marrow	15	0·9311–0·9380	31–29	37–45	199·0	55·4	1·1	—	—	—
	Bone	15	0·914–0·916	15–17	21–22	190·9	46–55·8	—	—	—	—
	Tallow, beef	15	0·943–0·952	35–27	45–40	193·2–200	38–46	0·25	95·6	40	49·0
	Tallow, mutton	15	0·937–0·953	36–41	44–45	192–195·2	35–46	—	95·5	—	—
Milk fat	Butter	15	0·926–0·940	20–23	28–33	227	26–38	12·5–15·2	86·5–89·8	40	41–4
	Stag	15	0·9670	39–48	49–52	199·9	20·5–25·7	1·66	—	40	44·5

European lards.

OILS.

Refraction		Variables		Characteristics of fatty acids									
Butyro-refractometer		Acetyl value	Acid value	Specific gravity		Solidifying point		Melting-point	Neutralisation value	Iodine value		Refraction	
°C.	Scale divisions		KOH mg.	°C.		°C.	Titre °C.	°C.	KOH mg.	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	11·6	—	—	—	—	—	—	—	—	—	—
—	—	—	4–21	—	—	—	—	—	—	—	—	—	—
—	—	13·0	10–35	—	—	—	28·2	—	—	—	—	—	—
25	78	—	—	—	—	—	—	—	—	—	197·4	—	—
—	—	—	1·8–44	—	—	—	—	—	178·5	—	—	—	—
—	—	—	21	—	—	—	—	—	181·5	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
25	75	4–8	1–25	—	—	—	18·4–24·3	21–25	204–207	130·5–170	—	60	1·4521
—	—	10·6	—	—	—	—	—	—	—	—	—	—	—
—	—	—	0·2–34	—	—	—	—	—	177·0	—	—	—	—
—	—	11·9	—	—	—	—	—	—	—	—	—	—	—
—	—	—	1·26–1·68	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	11·0	—	—	—	—	—	—	—	—	—	—
—	—	16·5	1·9–40	—	—	—	15·5–15·9	22–23	193·2	—	—	—	—
25	70	—	0·5–37	100	0·8922	—	2[illegible]·0	27·0	—	131·2	144·7	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	5·0	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	21·1	—	—	—	—	—	—
—	—	13·0	—	—	—	—	28·6	—	—	—	—	—	—
—	—	22·0	—	—	—	—	26·1–26·5	29·8–30·8	—	61·98–63·26	—	—	—
25	68·5	—	1·2	—	—	—	—	34–39	194·9	72·9	—	—	—

FATS.

Variables		Characteristics of fatty acids									
Acetyl value	Acid value	Specific gravity		Solidifying point		Melting-point	Neutralisation value	Iodine value		Refraction	
	KOH mg	°C.		°C.	Titre °C.	°C.	KOH mg	Total fatty acids	Liquid fatty acids	°C.	
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	5·9	15·0	0·9374	25–28	—	30–33	199·3	120·0	—	—	—
—	2·73	15·0	0·9361	36–40	—	44–47	209·0	93·3	—	40	Butyro-ref. 36
—	7·2	15·0	0·9246	35–36	—	39–41	209·5	101·1	—	—	—
—	6·2	15·0	0·9264	37–39	—	40–42	218·1	64·4	—	40	Butyro-ref 36
—	1·5	—	—	30–31	—	36–40	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	0–2·44	—	—	37·7	33·7	37·5–39·5	202·6	84–87	—	—	—
—	1·0	15·0	0·9182–0·9289	36–34	—	42–44	210·8–217·6	71·8–72·2	—	—	—
—	0·59	15·0	0·9257	31–32	—	38–40	202·4	65·3	—	—	—
—	0·86	15·0	0·9251	33–34	—	34–40	196·4	65·1	—	—	—
2·6	0·54–1·28	99·0	0·8445	39·0	41–42	43–44	201·8	64·0	92·1)[1] — 90–106)[2]	60 — 22	1·4395 Oleorefr. – 30
—	2·6	15·0	0·9333	32·5–33·5	—	39–40	203·6	81·2	—	—	—
4·2	1·6	15·0	0·9300–0·93[illegible]9	37·9–38	—	44–46	204·5	55·5	—	—	—
11·3	29·6–53	—	—	28·0	—	30·0	200·0	55·7–57·4	—	—	—
2·7–8·6	3·5–50	100·0 (100=1)	0·8698	—	37·9–46·2	43–44	197·2	41·3	92·4	60	1·4375
—	1·7–14	—	—	41·0	40, 15–48·2	49–50	210·0	34·8	92·7	60	1·4374
1·9–8·6	0·45–35·38	37·75 (15·5=1)	0·9075	33–38	—	38–40	210–220	28–31	—	60	1·437
—	3·5	15·0	0·9685	46–48	—	50–52	201·3	23·6	—	—	—

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[1] American lards.

J. L.

OILSTONE *v.* Whetstone.

OITICICA OIL. A drying oil extracted from the seeds of *Conepia grandifolia*, found in Brazil. The oil is present in the kernels to the extent of 62 p.c., is semi-solid at ordinary temperatures, and of a bright yellow when liquid. M.p. between 21·5° and 65·1°; iodine value, 179·5; saponification value, 188·6; free fatty acids, as oleic, 5·7; unsaponifiable matter, 0·91 p.c.; sp.gr. 0·9694 at 15·5°/15·5°. Rapidly absorbs oxygen from the air when liquid (Bolton and Revis, Analyst, 1918, 251).

OKRA, also called gumbo; *Hibiscus esculentus* (Linn.), an annual plant bearing edible pods. Zega (Chem. Zeit. 1900, 24, 871) found, as the average of 4 analyses—

Water	Protein	Fat	N-free extract	Fibre	Ash
80·7	4·2	0·4	12·1	1·2	1·4

According to American analyses (Bull. 28, U.S. Dept. of Agric. 1899), the edible portion of the pods, used largely as a vegetable in America, is much more watery, as shown by the following figures:—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
90·2	1·6	0·2	4·0	3·4	0·6

whilst, according to the same authority, canned okra contains—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94·4	0·7	0·1	2·9	0·7	1·2

(*v.* Tinsley, Amer. Chem. J. 1893, 14, 625).

H. I.

OLD FUSTIC is the wood of a tree known as the *Chlorophora tinctoria* (Gaudish), previously called *Morus tinctoria* (Linn.) which occurs wild in different tropical regions. The tree frequently grows to a height of over 60 feet, is exported in the form of logs, sawn straight at both ends, and usually deprived of the bark. The best qualities of old fustic come from Cuba and the poorer from Jamaica and Brazil. It is at the present time used very largely, and, together with logwood, is the most important of the natural dyestuffs.

The colouring matters of old fustic were first investigated by Chevreul (Leçons de chimie appliquée à la teniture, II. 150), who described two substances, one sparingly soluble in water, called *morin*, and a second somewhat more readily soluble. Wagner (J. pr. Chem. [i.] 51, 82) termed the latter *moritannic acid*, and considered that it possessed the same percentage composition as morin. Hlaziwetz and Pfaundler (Annalen, 127, 351), on the other hand, found that the so-called moritannic acid was not an acid, and as moreover its composition and properties were quite distinct from those of morin, they gave it the name of 'Maclurin.'

Morin $C_{15}H_{10}O_7,2H_2O$. To isolate this colouring matter from old fustic a boiling extract of the rasped wood is treated with a little acetic acid and then with lead acetate solution. This causes the precipitation of the morin in the form of its yellow lead compound, whereas the main bulk of the maclurin remains in solution. The washed precipitate in the form of a thin cream is run into boiling dilute sulphuric acid, and the hot liquid, after decantation from the lead sulphate, is allowed to stand. Crystals of crude morin are gradually deposited, and a further quantity can be isolated from the acid solution by means of ether. During the preparation of commercial fustic extract, the solution on standing, or the concentrated extract itself, deposits, as a rule, a brownish-yellow powder, which consists principally of a mixture of morin and its calcium salt, and this forms the best source for the preparation of large quantities of the colouring matter. The product is digested with a little boiling dilute hydrochloric acid to decompose the calcium compound, extracted with hot alcohol, and the extract evaporated. Crystals of morin separate on standing, and a further quantity can be isolated by the cautious addition of a little boiling water to the mixture.

Crude morin can be partially purified by crystallisation from dilute alcohol or dilute acetic acid, but the product usually contains a trace of maclurin. To remove the latter the finely powdered substance is treated in the presence of a little boiling acetic acid with fuming hydrobromic acid (or hydrochloric acid), which precipitates the morin as halogen salt, whereas the maclurin remains in solution (Bablich and Perkin, Chem. Soc. Trans. 1896, 69, 792). The crystals are collected, washed with acetic acid, decomposed by water, and the regenerated morin crystallised from dilute alcohol.

Morin crystallises in colourless needles (B. and P.) readily soluble in boiling alcohol, soluble in alkaline solutions with a yellow colour. Lead acetate solution gives a bright orange-coloured precipitate and ferric chloride an olive-green coloration.

Loewe (Zeitsch. anal. Chem. 14, 112) was the first to assign to morin the formula $C_{15}H_{10}O_7$, and that this was correct was shown by the analysis of its compounds with mineral acids (Perkin and Pate, Chem. Soc. Trans. 1895, 67, 649). The *hydrochloride*, *hydrobromide*, and *hydriodide* are obtained in orange-coloured needles, and possess the formulæ $C_{15}H_{10}O_7{\cdot}HCl$, $C_{15}H_{10}O_7{\cdot}HBr$, and $C_{15}H_{10}O_7{\cdot}HI$, but the sulphuric acid compound, known as *anhydromorin sulphate* $C_{15}H_8O_6{\cdot}H_2SO_4$, orange-red needles, is of an abnormal character. *Monopotassium morin* $C_{15}H_9O_7K$, yellow needles, *monosodium morin* $C_{15}H_9O_7Na$, *magnesium morin* $(C_{15}H_9O_7)_2Mg$, orange-yellow needles, and *barium morin* $(C_{15}H_9O_7)_2Ba$, orange crystalline powder, have also been prepared (Perkin, Chem. Soc. Trans. 1899, 75, 437).

When an alcoholic solution of morin is treated with bromine (Benedikt and Hazura, Monatsh. 5, 667; Hlaziwetz and Pfaundler, J. 1864, 557) it is converted into *tetrabrom-morin ethyl ether* $C_{15}H_5Br_4O_7Et,2H_2O$, colourless needles, m.p. 155° (Herzig, Monatsh. 18, 700), and this when digested with stannous chloride and hydrochloric acid gives *tetrabromo-morin* $C_{15}H_6Br_4O_7$, (B. and H.), colourless needles, m.p. 258°. According to Perkin and Bablich, this latter compound is more simply prepared by the direct bromination of morin suspended in acetic acid.

By the action of acetic anhydride, according to the usual methods, a colourless amorphous product results, and a crystalline pentacetylmorin has not yet been prepared. Cold acetic anhydride, however, converts the monopotassium salt of the colouring matter into *tetra-acetyl morin* $C_{15}H_6O_7(C_2H_3O)_4$, colourless prismatic needles, m.p. 142°–145°, but this on further acetylation gives an amorphous compound.

Tetrabromomorin, on the other hand, yields a *penta-acetyl derivative* (Bablich and Perkin) $C_{15}HBr_4O_7(C_2H_3O)_5$, colourless needles, 192°–194°, and it was subsequently found by Herzig that tetrabromomorin ethyl ether yields the compound $C_{15}HBr_4O_7Et(C_2H_3O)_4$, m.p. 116°–120°.

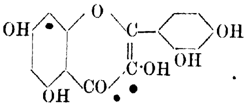
By fusion with alkali morin gives *phloroglucinol* (H. and P.), and *resorcinol* (B. and H.), whereas in this manner Bablich and Perkin isolated *β-resorcylic acid*. When methylated with methyl iodide *morin tetramethyl ether* $C_{15}H_6O_3(OCH_3)_4$ (B. and P.), yellow needles, m.p. 131°–132°, is produced, but is isolated with difficulty, and from this compound with alcoholic potash a yellow potassium salt, readily decomposed by water, is obtained. *Monoacetyltetramethylmorin* $C_{15}H_5O_3(OCH_3)_4C_2H_3O$, colourless needles, melts at 167°.

Morin tetraethyl ether $C_{15}H_6O_3(OC_2H_5)_4$ (Perkin and Phipps, Chem. Soc. Trans. 1904, 85, 61), yellow needles, m.p. 126°–128°, and *acetylmorintetraethyl ether*,

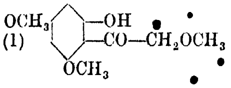
$$C_{15}H_5O_3(OC_2H_5)_4C_2H_3O$$

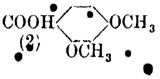
colourless needles, m.p. 121°–123°, could only be prepared in small quantity.

When *morin tetramethyl ether* is hydrolysed with alcoholic potash *β-resorcylic acid dimethyl ether*, and *phloroglucinolmonomethyl ether* are produced. Bablich and Perkin assigned to morin the constitution of a *pentahydroxyflavone* (tetrahydroxyflavonol)—



and that this formula correctly represents the substance, has been proved by its synthesis (Kostanecki, Lampe and Tambor, Ber. 1906, 39, 625), and also by the investigation of Herzig and Hofmann (Ber. 1909, 42, 155). It has been shown by the latter chemists that when morin is methylated by means of methyl sulphate, *morin pentamethyl ether* $C_{15}H_5O_2(OCH_3)_5$, needles, m.p. 154°–157°, can be produced, though for this purpose Perkin and Watson (Chem. Soc. Trans. 1915, 107, 207) prefer the modification of Valiaschko's process (Arch. Pharm. 1904, 242, 242), previously found serviceable for the preparation of quercetin pentamethyl ether by Watson. Morin pentamethyl ether is hydrolysed with boiling alcoholic potash into *β-resorcylic acid dimethyl ether* (2), and *methoxy fisetol trimethyl ether* (1) (*cf.* Quercetin and Fisetin)—





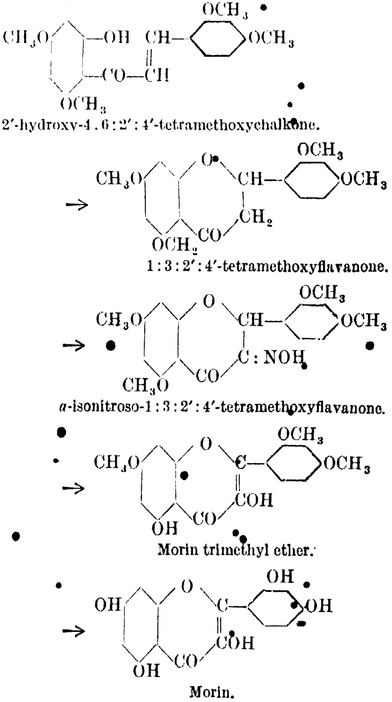
the latter being identical with the compound obtained in a similar way from quercetin pentamethyl ether.

By nitration it forms *nitromorin pentamethyl ether* $C_{15}H_4O_2(OMe)_5NO_2$, reddish-brown needles, m.p. 223°–225°, and this when reduced with alcoholic hydrochloric acid and tin gives *aminomorin pentamethyl ether*, colourless hexagonal plates, m.p. 204°–205°, the *platinichloride* $(C_{20}H_{21}O_7N)_2H_2PtCl_6$, of which forms stout yellow prisms. Attempts to prepare the hydroxy compound from this amino derivative were unsuccessful. *Aminomorin*

$$C_{15}H_4O_2(OH)_5NH_2$$

obtained from the nitropentamethyl ether with hydriodic acid is yellowish-brown and dissolves in alkalis to form a brownish-yellow solution. The hydriodide $C_{15}H_4O_2(OH)_5NH_2{\cdot}HI,H_2O$ crystallises in square platelets (Perkin and Watson).

Kostanecki, Lampe and Tambor (Ber. 1906, 39, 625) have synthesised morin by reactions similar to those found serviceable in the artificial preparation of fisetin and quercetin (*see* Young Fustic and Quercitron bark), but in this case the formation of the flavanone did not proceed smoothly and only a small quantity could be prepared. The synthesis is illustrated by the following formulæ—



2′-hydroxy-4.6:2′:4′-tetramethoxychalkone.

1:3:2′:4′-tetramethoxyflavanone.

a-isonitroso-1:3:2′:4′-tetramethoxyflavanone.

Morin trimethyl ether.

Morin.

Morin dyes mordanted woollen cloth shades which, though of a slightly stronger character, closely resemble those given by kaempferol.

	Chromium	*Aluminium*	*Tin*	*Iron*
Morin .	Olive yellow	Yellow	Lemon yellow	Deep olive brown
Kaempferol	Brown yellow	,,	Bright yellow	Deep olive brown

(Perkin and Wilkinson, Chem. Soc. Trans. 1902, 81, 590).

Maclurin $C_{13}H_{10}O_6$. When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the colouring matter. The crude product is crystallised from dilute acetic acid (Perkin and Cope). A crude maclurin is also obtained during the preparation of fustic extract, partially in the form of its calcium salt, and this product is treated with dilute hydrochloric acid and crystallised from water. In order to decolorise the crystals, acetic acid is added to a hot aqueous solution and a little lead acetate in such quantity that no precipitate is formed, and the solution is treated with sulphuretted hydrogen. The clear liquid is now much less strongly coloured, and after repeating the operation two or three times, the maclurin, which crystallises out on standing, possesses only a pale yellow tint.

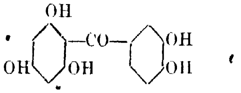
When quite pure maclurin consists of colourless needles, m.p. 200° (Wagner, J. 1850, 529), somewhat soluble in boiling water, soluble in alkalis with a pale yellow coloration. With aqueous lead acetate it gives a yellow precipitate and with ferric chloride a greenish-black coloration.

Hlasiwetz and Pfaundler (J. 1864, 558) assigned the formula $C_{13}H_{10}O_6$ to maclurin, and found that by boiling with potassium hydroxide solution it gives *phloroglucinol* and *protocatechuic acid*.

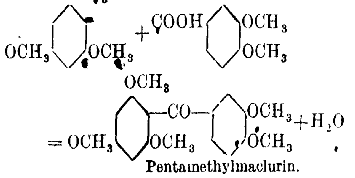
Pentabenzoylmaclurin $C_{13}H_5O_6(C_7H_5O)_5$ melts at 155°–156° (König and V. Kostanecki, Ber. 1894, 27, 1996); and *tribrom maclurin*

$$C_{13}H_7Br_3O_6,H_2O$$

colourless needles, has been obtained by Benedikt. *Maclurin pentamethyl ether* $C_{13}H_5O(OCH_3)_5$, colourless leaflets, melts at 157°. König and V. Kostanecki first assigned to maclurin the constitution of a *pentahydroxybenzophenone*—

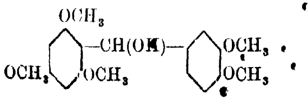


W. H. Perkin and Robinson (Chem. Soc. Proc. 1906, 22, 305), and somewhat later Kostanecki and Tamber (Ber. 1906, 39, 4022) synthesised maclurin pentamethyl ether, by the interaction of veratric acid and phloroglucinol trimethyl ether in presence of aluminium chloride—



Pentamethylmaclurin.

When maclurin pentamethyl ether is digested with alcoholic potash and zinc-dust *leucomaclurin-pentamethyl ether* (Kostanecki and Lampe, Ber. 1906, 39, 4014)



is produced in prismatic needles, m.p. 109°–110°, and this on further reduction gives *pentamethoxydiphenyl methane*, m.p. 107°–108°.

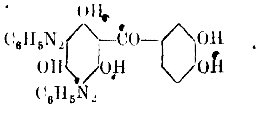
On the other hand, if leucomaclurin pentamethyl ether is oxidised in acetic acid solution, *veratric acid* and *dimethoxybenzoquinone* are formed.

Maclurin has been synthesised by Hoesch and Zarzecki (Ber. 1917, 50, 462, 660) by the condensation of protocatechuonitrile with phloroglucinol by means of zinc chloride in the presence of a current of hydrogen chloride, the ketone-imide being hydrolysed to maclurin by boiling with water.

Maclurin is interesting as it represents the only simple benzophenone colouring matter which is as yet known to exist in nature. It is possible, however, that kinoin from Malabar kino, and aromadendrin from eucalyptus kino also belong to this class (*v.* Kino).

Patent fustin. Under the name of 'patent fustin' a colouring matter has been placed on the market, which consists chiefly of disazobenzene maclurin (C. S. Bedford, 1887, Eng. Pat. 12667). To prepare this substance old fustic is extracted with boiling water, the solution is decanted from the precipitate of morin and its calcium salt which separates on cooling, and is neutralised with the necessary quantity of sodium carbonate. Diazobenzene sulphate is then added until a precipitate no longer forms, and this is collected and washed with water. It is sold in the form of a paste and dyes chrome mordanted wool an orange-brown shade.

Disazobenzene maclurin (Bedford and Perkin, Chem. Soc. Trans. 1895, 67, 933; *ibid.* 1897, 71, 186) which crystallises in salmon-red prismatic needles, m.p. 270° (decomp.) has the following constitution—



With acetic anhydride it gives *triacetyl disazobenzene maclurin* $C_{13}H_5O_5(C_6H_5N_2)_2(C_2H_3O)_3$, in orange-red needles, m.p. 240°–243° (decomp.).

Dyeing properties of old fustic.—In silk and cotton dyeing fustic is employed to a comparatively limited extent, but in wool dyeing it is the most important natural yellow dyestuff. The olive-yellow or old gold colours which fustic yields when used with chromium mordant and the greenish olives obtained with the use of copper and iron mordants are all fast to light and milling, but the yellow colours yielded in conjunction with aluminium and tin possess only a moderate degree of fastness with respect to light. Fustic is chiefly employed in wool dyeing with potassium dichromate as the mordant, and it is for the most part used along with other dyestuffs, *e.g.* logwood, alizarin, &c., for the production of various compound colours, olive, brown, drab, &c. A. G. P.

OLEANDER LEAVES. Oleander leaves contain substances having a digitalis-like action, which are readily soluble in water and in alcohol, and the solutions are stable. They probably consist of complex glucosides (Straub, Arch. Exp. Pathol. u. Pharmakol. 1918, 82, 327). *Cf.* art. Digitalis.

OLEANDRIN *v.* Digitalis.

OLEANODYNE. Trade name for a preparation containing oleic acid, aconitine, atropine, morphine, and veratrine.

OLEFIANT GAS *v.* Ethyl.

OLEFINES. Hydrocarbons of the C_nH_{2n} series homologous with ethylene.

OLEIC ACID *v.* Oils (Fixed) and Fats; Saponification.

OLEIN *v.* Oils (Fixed) and Fats; Glycerin.

OLEOGUAIACOL. Syn. for Guaiacol oleate.

OLEOMARGARINE *v.* Margarine.

OLEO-RESINS. Under the generic term oleo-resins are here described the chief representatives of that large group of natural products the essential constituents of which are resin and volatile oil. These substances are, for the most part, the oleo-resinous juices of plants more or less deprived of their volatile oil by evaporation, but still retaining enough for it to rank as one of their two leading components. For a more detailed list of oleo-resins, the numerous reports on botanical economics, and the catalogues of the various museums, should be consulted. Compare also the introduction to the article on Resins.

Copaiba; B. P., U.S. P. *Oleo-resin copaiba*; *Balsam of copaiba or copaiva or capivi*; (*Baume ou oléo-résine de copahu*, Fr.; *Copaiva balsam*, Ger.). Copaiba is the oleo-resinous secretion of the trees of the genus *Copaifera*, especially the species *C. Lansdorfii* (Desf.), which inhabit the warmer districts of South America. Descriptions of the leading species yielding the so-called balsam are given by Fluckiger and Hanbury (Fluck. a. Hanb. 227) and Bentl. a. Trim. 93. The drug became known in Europe in the seventeenth century, and was included in the Amsterdam Pharmacopœia of 1636 and the London Pharmacopœia of 1677. The yield of oleo-resin from a single tree is very great, the ducts containing it distending sometimes to such an extent as to burst the unyielding trunk with a report which is heard at long distances. In commerce the Pará variety is distinguished from that coming from Maranham and from the rarer Maracaibo copaiba.

In trade the oleo-resin occurs as a transparent, rarely opalescent, viscid liquid of a pale-yellow or light golden-brown colour, and a characteristic aromatic, not disagreeable, odour and persistent acrid bitterish taste. The specific gravity, which varies with the proportion of oil present, is generally 0·935–0·995 (0·940–0·995 at 25°, U.S. P.). Alcohol, benzene, carbon disulphide, or acetone dissolve most specimens of copaiba: glacial acetic acid dissolves the resin only. When mixed with small quantities of magnesia, lime, or baryta, most specimens form a stiff mixture which gradually hardens. This depends upon the presence of an acid resin which forms salts with alkaline earth metals. Flückiger (Jahresb. Pharm. 1867, 162; 1868, 140) finds the action of copaiba on polarised light to vary, some specimens being dextro- and others lævo-rotatory.

The *volatile oil* in copaiba varies from 20 to 80 p.c. (generally 40–60 p.c.), the percentage of *resins*, which are the sole other constituents, showing corresponding differences. A method for the estimation of the volatile oil is given by Cripps (Pharm. J. [iii.] 22, 193).

The U.S. P. requires a minimum content of 36 p.c. of resin and an acid value of 28–95 for copaiba.

Volatile oil of copaiba boils at 252°–260°, is soluble in 8–30 parts of alcohol (sp.gr. 0·830), or in 3 parts of absolute alcohol, and has a sp.gr. of 0·88–0·91. The oil has the odour and taste of copaiba, and consists principally of sesquiterpenes, largely *caryophyllene* $C_{15}H_{24}$, b.p. 258°–260° (Wallach, Annalen, 1892, 271, 294). When hydrogen chloride is passed into the dried oil, crystals of a *hydrochloride* $C_{15}H_{24},3HCl$, m.p. about 70° (*cf. e.g.* Deussen and Eger, Chem. Zeit. 1912, 36, 561). The terpene of Maracaibo copaiba boils at 250°–260°, and gives no crystalline hydrochloride (Brix, Monatsh. 2, 507). A dark-blue *hydrate* $(C_{20}H_{32})_3,H_2O$ is obtained towards the end of the operation when the moist terpene is distilled over sodium (Brix).

The oil from copaiba balsam collected in Surinam from *Copaifera guyanensis* (Desf.) boils, for the most part, at 254°–262°, and appears to be a mixture of two *sesquiterpenes*. The fraction boiling at 270°–280° contains a little cadinene. Towards the end of the steam distillation of the balsam, a *sesquiterpene alcohol* $C_{15}H_{26}O$, m.p. 114°–115°, separates in the condenser from which a *sesquiterpene* $C_{15}H_{24}$, b.p. 252°, is obtained. The latter is a mobile liquid which soon changes in the air to a resinous solid (van Italie and Nieuwland, Arch. Pharm. 242, 539; 244, 161).

Of the copaiba resins many are found only in certain varieties of the oleo-resin. The most important is the crystalline acid resin *copaivic acid* $C_{20}H_{30}O_2$. This constitutes by far the greater portion of the crude resin, and may be obtained according to Schweitzer (Pogg. Ann. 17, 784; 21, 172) by steam distilling the balsam and then allowing an alcoholic solution of the resin, so obtained, to evaporate spontaneously. It may also be extracted from the balsam by aqueous ammonium carbonate solution, and may be crystallised from alcohol; m.p. 131°. The acid is an isomeride of abietic acid. Crystalline deposits sometimes occur in copaiba. One of these, in an old specimen of the Trinidad variety, which was supposed to be copaivic acid, was examined by Flückiger and Hanbury (Flück. a. Hanb. 231). It melted at 116°–117°. Another deposit investigated by Fehling (Annalen, 40, 110) proved to be an allied compound *oxycopaivic acid* $C_{20}H_{28}O_3$. Similarly, Strauss (*ibid.* 148, 148) extracted *metacopaivic acid* $C_{22}H_{34}O_4$ from Maracaibo copaiba. Copaiba from Maracaibo and Pará has been examined by Tschirch and Keto (Arch. Pharm. 239, 548). After separation of the resin acids and the essential oil, a small quantity of a mixture of indifferent *resenes* remained mostly, but not wholly, soluble in alcohol. From the Para balsam, *paracopaivic acid* $C_{20}H_{32}O_3$, m.p. 145°–148°, extracted by 5 p.c. ammonium carbonate solution, and *homo-paracopaivic* acid $C_{18}H_{28}O_3$, m.p. 111°–112°, were obtained. From samples of Maracaibo copaiba, *β-metacopaivic acid* $C_{11}H_{16}O_2$ (or $C_{16}H_{24}O_3$), melting at 89°–90°, and *illuric acid* $C_{20}H_{28}O_3$, melting at 128°–129°, were isolated. Other resins have been described by Martin and Vigne (J. Pharm. Chim. [iii.] 1, 52), Posselt, (Annalen, 69, 67), and Rush (Amer. J. Pharm. [iv.] 9, 305). *Cf.* Oberdöfer (Arch. Pharm. [ii.] 44, 172); Ulek (*ibid.* 122, 14); Procter (Pharm. J. [iii.] 10, 603); Roussin (J. Pharm. Chim. [iv.] 1, 321); Levy (Ber. 18, 3206).

Illurin oleo-resin, an African variety of copaiba, obtained from *Hardwickia Mannii* (Oliver) in the Niger basin, also examined by Tschirch and Keto, contains *illuric acid* which closely resembles Fehling's oxycopaivic acid. It crystallises in the hexagonal system and is a monobasic acid. It gives the cholesterol reactions and is not affected by fusion with potassium hydroxide; in these and other respects, it resembles the resin acids of the coniferæ, especially pimaric acid, but it differs from them by reducing silver salts in ammoniacal solution.

In medicine, copaiba is employed for its stimulating action on mucous membranes, especially those of the genito-urinary system.

Adulteration of copaiba has been largely practised. Turpentine, castor oil, and gurjun 'balsam' are typical of the adulterants employed. Numerous methods of testing have been proposed. These are reviewed in Allen's Commercial Org. Analysis, 4th ed. vol. iv. p. 88; vol. ix. p. 313. It is shown that the specific gravity or percentage of resin and oil is so variable as to be of no value in detecting adulteration. Many properties while appertaining to most specimens of the oleo-resin are not found in all. Thus fluorescence, a character of gurjun 'balsam,' is not absent from all specimens of true copaiba; all specimens do not dissolve one-fourth of their weight of magnesium carbonate or form a clear solution with aqueous ammonia or alcohol. Benzene is a universal solvent for copaiba, but it behaves in the same manner toward all the ordinary adulterants. Siebold (Pharm. J. [iii.] 8, 251) detects as little as 1 p.c. of fatty oil in a simple manner. A gram or so is heated in a watch-glass until all oil is driven off, which is the case as soon as the residue assumes a rich brown colour. If the remaining resin is brittle and pulverisable, no fatty oil is present; fatty oils cause the residue to remain sticky, even after further heating. Gurjun or wood oil may be discovered by Flückiger's process (Fluck. a. Hanb. 233 note). One drop of copaiba is agitated in a test tube with 19 drops of carbon disulphide, and to this is added a drop of a mixture of equal volumes of strong sulphuric and nitric (1·42) acids. After a little agitation, copaiba becomes reddish-brown with a deposit of resin on the sides of the tube; gurjun oil gives an intense purplish-red colour changing to violet, whilst the oleo-resin of *Hardwickia*, sometimes an adulterant of copaiba, gives no perceptible alteration of colour. By this procedure, 1 part of gurjun oil in 8 parts of copaiba may be detected. Another method is that of Hager (Pharm. Centh. 16, 257). 1 volume of copaiba mixed with 4 volumes of light petroleum gives either a clear solution or only a slight turbidity which, when it settles, forms not more than a thin film covering the bottom of the vessel. Gurjun oil is insoluble in light petroleum and settles in half an hour. Benzene cannot be substituted, as has been proposed, for light petroleum. Gurjun balsam can also be detected in copaiba by giving a reddish coloration, changing to blue, when the sample is boiled with 3 parts of 95 p.c. alcohol and 1 part of crystallised stannous chloride, and by affording a reddish or purple colour when 4 drops of copaiba are carefully added to a mixture of half an ounce glacial acetic acid with 4 drops of nitric acid (*cf.* Brit. Pharm.). According to Turner (Amer. J. Pharm. 1908, 80, 14) 3–4 drops of the volatile oil are mixed with 3 c.c. of glacial acetic acid, and 1 drop of freshly prepared 10 p.c. sodium nitrite solution. On pouring 2 c.c. of sulphuric acid below this, without mixing, the acetic layer is at most coloured pale yellow and pink, red or violet (absence of gurjun balsam, *q.v.*). The presence of oil of turpentine is recognised by Siebold during the evaporation for the detection of fixed oils, and may be further identified by distillation and fractionation of the volatile oil. Turpentine boils at 160°–180°, oil of copaiba at 240°–250°. See further: Bowman (Amer. J. Pharm. [iv.] 7, 385); Fulton (*ibid.* [iv.] 7, 550); Rush (Pharm. J. [iii.] 10, 5); Hager (Pharm. Centh. 1870, 296; 24, 141); Prael (Arch. Pharm. [iii.] 23, 735, 768); Wzyne (Amer. J. Pharm. [iv.] 3, 326); Maupy (Chem. Zentr. 1894, i. 929); Hirschsohn (*ibid.* 1895, ii. 694).

Elemi. *Oleo-resina elemi* (*Résine elémi*, Fr.; *Elemiharz*, Ger.). The Greek and Roman writers describe a 'gum of Ethiopian olive' which has been generally identified with elemi. According to Fluckiger and Hanbury (Flück. a. Hanb. 147), however, this ancient elemi is the oleo-resin known as *Luban meyeti*. Pliny terms the drug *enhæmon* or *enhæmi*, from which the name *animi* and perhaps also *elemi* is derived. The term 'animi' is also used for a kind of copal.

During the sixteenth century, the older African elemi was replaced by a drug of similar appearance, which came from Mexico, and South America, and this in its turn has given way to a product of the Philippine Islands, which is now the elemi of commerce.

Elemi or Animi of the older Writers; Oriental or African Elemi; Luban Meyeti; Luban Mati.

This drug is derived from *Boswellia Frereana* (Birdwood), a tree belonging to the same genus which yields the gum-resin olibanum, and which inhabits the hills immediately west of Cape Gardafui. Notwithstanding the close botanical relation to olibanum, and the generic name, Luban being Arabic for that drug, there is no doubt, owing to the entire absence of gum and other characters, that Luban Meyeti is a distinct product. According to Hanbury and Flückiger (Pharm. J. [iii.] 8, 805; Flück. a. Hanb. 147), this was the elemi of commerce until its place was taken, in the sixteenth century, by a somewhat similar product of Mexico and South America.

Luban elemi is described by Flückiger and Hanbury as detached droppy tears and fragments, occasionally in stalactitic masses several ounces in weight. Externally it has a thin opaque white crust, but internally it is transparent and of an amber colour. It has an agreeable odour of lemon and turpentine, and a mild terebinthinous taste. The *volatile oil*, which has a fragrant elemi odour, from the specimen examined, amounted to 3·1 p.c. It has a specific gravity of 0·856 at 17°, and rotates the polarised ray slightly to the left. It consists partly of a dextro-rotatory *hydrocarbon* $C_{10}H_{16}$, and partly of a lævo-rotatory *oxygenated oil*. The *resin* is mostly soluble in alcohol, and has the composition $C_{20}H_{30}O_2$ (?).

Elemi of the Seventeenth and Eighteenth Centuries; American or Brazilian Elemi.

The oleo-resin, which replaced the older African elemi for the most part during the seventeenth and eighteenth centuries, was the product of several Brazilian trees, species of the genus *Protium* (*Icica*). A specimen examined by Flückiger and Hanbury (Flück. a. Hanb. 152), was a translucent greenish-yellow fragrant terebinthinous resin, which by means of cold alcohol could be separated into two portions—the one soluble, and the other, consisting of a mass of acicular crystals, insoluble.

The oleo-resin of *Protium heptaphyllum* (March.), was examined by Stenhouse and Groves (Chem. Soc. Trans. 29, 175). This is known as *Gum Hyawa*, or *Conima resin*, or *resin of the incense-tree*. It possesses a fragrant balsamic odour, which depends on the presence of a small proportion of *volatile oil*. This oil, when obtained by distillation with steam, boils at about 270°. By treatment with sodium and fractional distillation, it gives a hydrocarbon *conimene*, $C_{15}H_{24}$, which boils at 264°. If the residue, after removal of the volatile oil, be dissolved in hot alcohol, it deposits on cooling a crystalline compound, *icacin*, $C_{46}H_{76}O$ (?) and the mother-liquor contains a yellow *amorphous resin*. Icacin melts at 175° (*cf.* Hesse, Annalen, 192, 181), and is doubtless identical with *Amyrin* (*see* below).

Elemi of Commerce of the Present Day; Manilla Elemi; Arbol a Brea Resin.

The tree which yields the elemi of the present day is a native of the Philippine Islands, and is called by the Spaniards *Arbol a brea*. Its botanical relations were not known until quite recently, but it is now certain that the oleo-resin is collected from *Canarium luzonicum* (Miq.) (Clover, Philippine J. Sci. 1907, 2, 2). Manilla elemi is a soft oleo-resin which, in appearance, resembles old honey. It occurs in commerce generally admixed with earthy or carbonaceous matter, which gives it a dark colour. When fresh and pure, it is colourless and has a fragrant odour. Cold alcohol applied to the drug discloses numerous acicular crystals visible under a microscope (Flück. a. Hanb.).

Elemi is a mixture of *volatile oil* and *resin*. The volatile oil (up to 30 p.c.) contains *d*-phellandrene, dipentene, and a crystalline compound which may be identical with amyrin (Wallach, Annalen, 252, 102). Phellandrene and dipentene are also obtained by the dry distillation of the resin (Wallach, *ibid.* 271, 310). From the highest boiling fractions, Semmler (Ber. 1908, 41, 1768; 1918, 2183) has isolated *elemicin* or 1-allyl-3:4:5-trimethoxybenzene, b.p. 144°–147°/10 mm., and Semmler and Liao (*ibid.* 1916, 49, 794; 1917, 50, 1286) have further obtained *elemol*, $C_{15}H_{26}O$, b.p. 152°–156°/17 mm., yielding the sesquiterpene elemene, b.p. 115°–156°/10 mm. on dehydration.

All elemi resins are characterised by their high content of crystalline substances, the chief being a phytosterol; Baup (Ann. Chim. [iii.] 31, 108) called the latter *amyrin*. It is insoluble in water, readily soluble in ether and hot alcohol, and crystallises in satiny fibres, which melt at about 175°. Amyrin, $C_{30}H_{50}O$, has been converted by Vesterberg into two crystalline isomeric acetates, $C_{30}H_{49}(C_2H_3O_2)$, and benzoates, $C_{30}H_{49}(C_7H_5O_2)$, from which two corresponding amyrins have been prepared. α-*Amyrin* melts at 181°–118·5°, (α)-*amyrin acetate* at 220°, and *benzoate* at 192°; while β-*amyrin* melts at 193°–194°, (β)-*amyrin acetate* at 235°, and *benzoate* at 230° (Ber. 20, 1243; 23, 3186). Ciamician (Ber. 11, 1347), by distilling amyrin with zinc-dust, obtained toluene, methylethylbenzene, and ethylnaphthalene. The cinnamate of α-amyrin occurs in the latex of *Antiaris toxicaria* (Windaus and Welsch, Arch. Pharm. 1908, 246, 564), and probably also in various guttaperchas from New Guinea (van Romburgh, Ber. 1904, 37, 3440; *cf.* Vesterberg, *ibid.* 1906, 39, 2467). Amyrin seems to be a triterpene alcohol. The alcoholic mother-liquor contains the *amorphous resin*, or resin soluble in cold alcohol, which is the largest constituent of elemi. Besides amyrin, Baup describes three other compounds occurring in elemi—*breidin*, *brein*, and *bryoïdin*. Of these the former has not been found again; the second is a diatomic alcohol of the probable formula $C_{30}H_{48}(OH)_2$, which differs from that of amyrin by one oxygen atom; m.p. 217° (Vesterberg, Ber. 1906, 39, 2467; this paper gives references to previous chemical examinations of elemi). For the third substance, *Cryoidin*, *see* below.

Specimens of Manila elemi have been examined by Tschirch and Cremer (Arch. Pharm. 240, 293). 100 parts of the drug contain: *manamyrin*, consisting of α and β amyrin, 20–25; essential oil, 20–25; *bryoïdin*, 0·8–1; α-*manelemic acid*, 5–6; β-*manelemic acid*, 8–10; *maneleresene*, 30–35; inorganic constituents and bitter substance, 1–2; impurities, 5–6 parts. Bryoïdin, $C_{21}H_{42}O_3$, m.p. 135·5°, was prepared by digesting the elemi with dilute alcohol at a gentle heat and evaporating the extract to crystallisation. It is neutral, has a bitter taste, and, whilst insoluble in cold water, dissolves readily in hot water and in alcohol and ether (Pharm. J. [iii.] 5, 142). α-Manelemic acid $C_{37}H_{56}O_4$, m.p. 215°, previously isolated by Buri (Pharm. J. [iii.] 8, 601), crystallises from the alcoholic solution of the acids, extracted from the resin by aqueous potassium carbonate, while the mother liquor contains amorphous β-manelemic acid $C_{44}H_{80}O_4$, m.p. 75°–76°. Maneleresene $C_{15}H_{30}O$ remains after the removal of the other constituents of the oleo-resin; it is amorphous and melts at 63°–65°.

Elemi is seldom used in medicine in this country. It is, however, sometimes employed in the form of ointment as a dressing for indolent ulcers. At present its chief use is in the preparation of printing inks, and occasionally as an ingredient in varnishes.

Oleo-resins allied to Elemi.

Anime.—Much confusion exists as to the use of the word anime, and the same may be remarked of tacamahac. By some writers anime is used as synonymous with elemi, and by others it is restricted chiefly to a variety of copal. There are, however, a number of other oleo-resinous products which are usually known as anime. The chief members of this class are: 1. *Gomart oleo-resin*, or *gommier resin*, the exudation of *Dacorydes hexandra* (Griseb.), an inhabitant of the West Indies (Imp. Inst. Rep. No. 63, 192). This has an odour between that of elemi and turpentine. Owing to its general resemblance to true elemi, gommier resin is commonly known as 'dry' or West Indian elemi. For analysis and commercial valuation, *see* Imp. Inst. Report. The oleo-resin has been examined by More (Chem. Soc. Trans. 75, 718). The essential oil was found to contain 64 p.c. of *l*-pinene and 17 p.c. of sylvestrene, and from the resin a crystalline compound, m.p. 166°-167°, was obtained, having the composition $C_{25}H_{44}O$. 2. *Brazilian anime*, the product of *Hymenæa courbaril* (Linn.), a tree belonging to the natural order *Leguminosæ*. The oleo-resin resembles mastic. It softens in the mouth, and when warmed emits a peculiar odour. The volatile oil is colourless, with a strong, not unpleasant odour and burning taste. It is completely soluble in alcohol (Paoli, Brugn. Giorn. 16, 326). After removal of the oil, cold alcohol extracts an *amorphous resin*, and the residue, dissolved in boiling alcohol, deposits on cooling a *semi-crystalline compound*, which was analysed by Laurent (Ann. Chim. [ii.] 66, 314). *See also* Batka (Pharm. J. [iii.] 6, 742); Guibourt (Rév. scient. 16, 177); Filhol (J. Pharm. Chim. [iii.] 1, 301, 507); Hancock (Ed. N. J. Sc. 1, 240); Manzini (J. Pharm. 27, 752); Deville (Annalen, 71, 354).

Carana.—A soft oleo-resin allied to Brazilian elemi, probably derived from *Protium Carana* (March.) and allied species. It has a fragrant balsamic odour and somewhat bitter taste. It contains 96 p.c. of resin, soluble in alcohol (Pelletier, Bull. Pharm. 4, 241). Carana elemi from *Protium Carana* (March.), has been examined by Tschirch and Saal (Arch. Pharm. 241, 149), who found that in 100 parts of the drug there were contained iso*carelemminic acid*, 2; *careleminic acid*, 8; *carelemic acid*, 10; essential oil, 10; amyrins, 20–25; resene, 30–35; impurities, 12–15 parts. For analytical constants *v.* Dieterich (Pharm. Centh. 40, 453).

Ceradia.—The product of *Ceradia* (*Othonna*) *furcata* (Lindl.). It is an amber-coloured oleo-resin with the odour of elemi (R. Thomson, Phil. Mag. 28, 422).

Mauritius elemi.—An oleo-resin very closely resembling Manilla elemi. It is the yield of the *Canarium mauritianum* (Blume; Fluck. a. Hanb. 152). It has been examined by Tschirch and Saal (Arch. Pharm. 1904, 242, 348). 100 parts of the drug were found to contain α-iso*colelemic acid*, 10; *coleleminic acid*, 2; β-iso*colelemic acid*, 8; *colamyrin*, 25-30; *coleresene*, 30-35; essential oil, 3; bitter principle and bryoidin, plant remains and impurities, about 10 parts.

Mexican elemi. Vera Cruz elemi.—Mexican elemi is not now an article of commerce. It is nearly related to Brazilian elemi. It is the reputed product of *Amyris Plumeri* (DC.); (Flück. a. Hanb. 152). This elemi has been examined by Tschirch and Cremer (Arch. Pharm. 1902, 240, 293), who find that it contains a very large proportion of substances which resist the action of alkalis (resene and amyrin) and this would make it peculiarly suitable for the basis of a lacquer.

Tacamahac.—The following are the more important oleo-resins which have been described as tacamahac: 1. *East Indian tacamahac*, the product of *Calophyllum inophyllum* (Linn.), which inhabits Bourbon and Madagascar. It is a dark-green balsamic resin—sp.gr. 1·032; m.p. 75°. 2. *Yellow tacamahac*, the exudation of *Amyris tacamahac* (Batka). It was labelled *Tacamahaque vierge* by Des Marchais, *African incense* by Pereira, and *Bdellium d'Afrique* by Guibourt. It melts at 100°, exhaling an agreeable odour, and the resin remaining is partly soluble in alcohol. The part insoluble in alcohol consists of yellow crystals—*tacamahacin*. This substance is insoluble in ether, sparingly soluble in alcohol, and is unaffected by alkalis or nitric acid. Sulphuric acid dissolves it with a violet colour (Batka, Pharm. J. [iii.] 6, 742). Yellow tacamahac is often termed anime. 3. *Oleo-resin of Protium heptaphyllum* (Aub.). This has been already described under the name of *conima resin* (*see Elemi of the seventeenth and eighteenth centuries*). A number of samples of Tacamahac resin have been examined by Tschirch and Saal (Arch. Pharm. 1904, 242, 365, 395), and analytical constants are given by Dieterich (Pharm. Centh. 40, 453).

Besides these, which Batka regards as true tacamahacs, the product of *Protium obtusifolium* (March), the *Mauritius tacamahac*, and common *galipot* of *Pinus Pinaster* (Soland), the latter under the name of the *bitter tacamahac of trees*, have been described as varieties of that drug.

Gurjun oleo-resin. *Gurjun balsam*; *Wood oil*, *Oleo-resina dipterocarpi*. This oleo-resin resembles and is used as an adulterant and substitute for copaiba (so called East Indian copaiba). It is obtained from Burma and the Straits, being the product of various species of *Dipterocarpus* (Flück. a. Hanb. 88). Gurjun oil must not be confounded with the fatty oil which is also known as wood oil, or *wood oil of China*, which is expressed from the seeds of the *Aleurites cordata* (Steud.), the well-known *Tung* tree of the Chinese.

Gurjun, or wood oil, resembles copaiba in appearance, with the exception of its fluorescence, a character rarely found in copaiba. When heated in a closed tube to 220° it becomes almost solid, whereas copaiba similarly heated does not lose its fluidity. For other distinguishing characters *v.* COPAIBA.

According to Semmler and Jakubowicz (Ber. 1914, 47, 1141, where *see* other references), gurjun oil contains two tricyclic sesquiterpenes, a lævo-rotatory one (67 p.c.) which gives Turner's reaction (*v.* COPAIBA), and a dextro-rotatory one (33 p.c.) which does not give it. The oil boils mostly at 255°–260°, and has D. 0·915–0·925.

When the resin of wood oil is extracted by alcohol, and aqueous solution of ammonia added and the *amorphous resin* which separates collected, the solution contains *ammonium gurjunate* from which gurjunic acid is obtained as a precipitate on the addition of a mineral acid, and it may then be recrystallised from ether or alcohol. Werner found it to melt at 220°, and to boil with decomposition at 260°. Gurjunic acid is soluble in alcohol, benzene and carbon disulphide. It may be regarded as tri-hydrated abietic acid thus: $C_{14}H_{64}O_5,3H_2O$. This formula agrees equally well with Werner's data. It is probably identical with the meta-copaibic acid of Strauss (*v.* COPAIBA). A *compound*, $C_{20}H_{30}O_2$, yielding a diacetate is obtained from gurjun oleo-resin and enters commerce as 'copaivic acid.' It is crystalline, melts at 126°–129°, is soluble in alcohol and ether but insoluble in water and alkalis (Brix, Monatsh. 2, 516). The amorphous resin which constitutes the chief part of the resin of wood oil consists of *gurjoresene* $C_{17}H_{28}O_2$, m.p. 40°–43° (Tschirch and Weil, Arch. Pharm. 1903, 241, 372). The deposits, largely crystalline in character, which are found in various samples of gurjun balsam, consist of resin alcohols or resin phenols, but are insoluble in alkalis, in these respects resembling amyrin.

In addition to its use as a substitute for copaiba, wood oil is employed in India as a natural varnish, especially for ships.

Ladanum; *Labdanum*. A sticky, black-brown, soft oleo-resin, derived from *Cistus polymorphus* (Willk.) and other species of *Cistus*, inhabiting the Grecian Archipelago and the shores of the Mediterranean (*cf.* Bentl. a. Trim. 24). It is a variable mixture of resin, volatile oil, gum, wax, and earthy and woody impurities. The odour is fragrant, and it has a bitter taste. Guibourt (Hist. Drogues, 3, 601), Pelletier (Bull. Pharm. 4, 503), Johnston (Phil. Trans. 1840, 344), Thiselton Dyer (Pharm. J. [iii.] 15, 301; 16, 385, 779). For analytical constants, *see* Dieterich (Pharm. Centh. 40, 453). For an account of the different commercial forms of ladanum, its history, mode of collection, properties and uses, *see* Holmes, Perfumery and Essent. Oil Record, 1911, 2, 132. The yellow oil (0·7–0·9 p.c.) boils at 50°–185°/15 mm., and contains alcohols, phenols, esters, terpenes, acetophenone, and 1 : 1 : 5-*trimethylcyclohexanone* (Masson, Compt. rend. 1912, 154, 517). According to Roure-Bertrand it possesses the following characters: d^{20} 0·9033, $[\alpha]_D^{17}$ −12° 10′; $n_D^{12·2}$ 1·4800; acid number 3·7; sapon. number 22·37; ester number 18·67; solubility in 90 p.c. alcohol 0·5 to 5·0 volumes.

Lupulin. *Lupulinic glands*; *Lupulina* (*Lupuline*, Fr.; *Hopfendrüsen*, *Hopfenstaub*, Ger.). The detached minute glands of the strobile of *Humulus lupulus* (Linn.) contain *volatile oil*, a *bitter acid*, *resin*, *wax*. *Humulus*, U.S. P. Hops and lupulin have been deleted from the B.P. 1914.

Cf. myrcene, ι-α-caryophyllene (together 80–90 p.c.) linalool, linaloyl *iso*nonate, probably traces of a geraneolester and a little of a diterpene (Chapman, Chem. Soc. Trans. 1903, 83, 505). The identity of the myrcene was proved by Semmler (Ber. 1911, 44, 2009); ι-α-caryophyllene was identified with Chapman's 'humulene' by Deussen (J. Prakt. Chem. 1911, [ii.] 83, 483).

Commercial lupulin has been examined by Barth (Chem. Zentr. 1900, [ii.] 681), who found it to contain 18·27 p.c. of ash, 63·93 p.c. of material soluble in ether, and 36·07 p.c. of lupulin husks. The portion soluble in ether contained 0·18 p.c. of wax, 11·55 p.c. of *α-resin*, 43·31 p.c. of *β-resin*, 0·17 p.c. of ash, and 8·72 p.c. of fat oil, *γ-resin*, &c. The proportion of sand in commercial lupulin varies from 10·9 to 20·2 p.c.

The volatile oil which exists to the extent of about 0·9 p.c. (Flück. a. Hanb. 553), consists according to Wagner (J. 1853, 516) and Personne (J. Pharm. Chim. [iii.] 26, 241, 321; 27, 22; J. 1854, 654) of a *terpene*, $C_{10}H_{16}$, boiling at 175°, and an oxygenated compound probably *valerol*, $C_6H_{10}O$, which boils at 210° and on oxidation yields *valeric acid*. The latter acid has also been detected in hops. The crude oil boils from 140° to 300°. *Cf.* Méhu (Thèse, Montpellier, 1867), and Ossipow (J. pr. Chem. [ii.] 28, 448) Chapman (Chem. Soc. Trans. 67, 54, 780) finds that the oil can be separated into two fractions: one, boiling at 166°–171°, probably a mixture of two *hydrocarbons*, $C_{10}H_{16}$ and $C_{10}H_{18}$, and the other, a sesquiterpene, *humulene*, $C_{15}H_{24}$, b.p. 160°–170° (60 mm.). The latter gives a crystalline, nitrosochloride melting at 164°–165°.

The resins present in lupulin are divided into soft and hard resins, according as they are soluble or insoluble in light petroleum (Hayduck, Bied. Zentr. 1887, 694). The α-resin, a soft resin precipitated by lead acetate, contains *α-lupulinic acid*, which, when pure, is extremely resistant to chemical reagents but is rapidly transformed into a resin at a high temperature (Barth, Chem. Zentr. 1900, [ii.] 915; Siller, Zeitsch. Nahr. Genussm. 18, 241). The β-resin, which is also a soft resin, is not precipitated by lead acetate. It appears to be an oxidation product of an organic acid, *β-lupulinic acid*, first obtained from hops by Bungerer (Bull. Soc. chim. [ii.] 45, 489) To prepare lupulinic acid, lupulin is extracted with light petroleum and the crude crystals which are obtained on concentrating the solution are purified by recrystallisation from alcohol and afterwards from light petroleum. The acid crystallises in glistening prisms which melt at 92° and become resinous on exposure to air (Barth and Lintner, Ber. 31, 2022). The γ-resin is insoluble in light petroleum. Siller (*l.c.*) finds it to be a mixture of at least two distinct resins differing in carbon content and in solubility in ether.

For estimation of the resins and their bitterness ($\alpha : \beta : \gamma = 10 : 7 : 4$), *see* Schmidt, Winge and Jensen (Compt. rend. Lab. Carlsberg, 1914, 11, 116).

Humulon = 'α-Hopfenbittersäure' = 'α-lupulinic acid,' was finally purified as a crystalline compound $C_{21}H_{30}O_5,C_6H_4(NH_2)_2$ with *o*-phenylene diamine by Wollmer (Ber. 1916, 49, 780). Humulon, $C_{21}H_{30}O_5$ when pure is quite stable and odourless, and almost tasteless. Several crystalline derivatives and fission products have been obtained. For other constituents of hops, *see* Power, Tutin and Rogerson (Chem. Soc. Trans. 1913, 103, 1286); Chapman (*ibid.* 1914, 105, 1895).

Mecca or **Opobalsam.** *Balm of Gilead.* This oleo-resin is the balm of the Old Testament and the Greek writers, and is the substance to which the name 'balsam' was originally applied. The term has, however, with the advance of discovery, come to have another meaning, and is now employed in a generic sense for those resins, oleo-resins, or gum-resins which contain cinnamic, or benzoic acids (compare BALSAMS). Mecca oleo-resin is the product of *Commiphora opobalsamum* (Engl.), a tree growing in Arabia. Trommsdorff (N. J. T. 16, 62) finds it to consist of *volatile oil*, 30 p.c.; *soft resin insoluble in alcohol*, 4 p.c.; *hard resin soluble in alcohol*, 64 p.c. A specimen analysed by Bonastre (J. Pharm. 18, 95) contained only 10 p.c. of volatile oil, and the other constituents were correspondingly higher. In physiological action, the oleo-resin is allied to copaiba and the turpentines.

Hardwickia pinnata Oleo-resin. This oleo-resin is an Indian substitute for copaiba. It is derived from a tree nearly related to the *Copaifera*, which inhabits the forests of South Travancore Ghats and South Canara. A specimen examined by Fluckiger and Hanbury (Fluck. a. Hanb. 233) was a thick, black-looking, viscid fluid, which, when viewed by transmitted light in thin layers, was yellow-green or vinous red, according to the thickness. It had no fluorescence, nor was it gelatinised by heating, as is the case with wood oil. Broughton (Beddowe, Flora Sylv. S. India, Madras, 1872, 255) found 25 to 40 p.c. of *volatile oil* $(C_5H_8)_n$, boiling at 225°. From the resins this observer was unable to prepare copaivic acid.

Minjak-lagam. An oleo-resin resembling gurjun was examined by Haussner (Arch. Pharm. 21, 241). It is dingy green by reflected and yellow by transmitted light. It is soluble in alcohol, ether, benzene, chloroform, or carbon disulphide, and yields 33 p.c. of *volatile oil* $C_{20}H_{32}$, boiling at 250°. The *resin* is composed of an acid $C_2H_{24}O_3$ and a neutral constituent.

Sumbul oleo-resin (*Racine de sumbul*, Fr.; *Sumbulwurzel*, *Moschuswurzel*, Ger.). The root of *Ferula Sumbul* (Hooker), or musk root (Bentl. a. Trim. 131), a perennial plant, inhabiting the mountains of Maghian, in the Khanate of Bokhara, is official in the United States (*Sumbul*, U.S. P.). It was deleted from the B.P. in 1914. When extracted with ether it yields about 9 p.c. of a *resin*, having a musky odour and ¼ p.c. of a bluish *volatile oil*.

Reinsch (Jahrb. pr. Pharm. 6, 300; 7, 79; 13, 68) obtained *sumbulamic* acid, a turpentine-like mass, which assumes the form of soft yellow needles on standing, and *angelic* acid. Compare also Reinsch. and Riecker (Jahrb. pr. Pharm. 16, 12). Sommer (Arch. Pharm. 138, 1) investigated sumbul root. On dry distillation, the oleo-resin gives first a *greenish mobile oil*, smelling like creosote, then a *blue oil*, lighter than water, and with a peculiar, not very agreeable, odour. Together with these, the same observer found crystals of *umbelliferone*.

Turpentine. The oleo-resinous exudates of various species of *Coniferæ*.

Crude or common turpentine. This is derived in Russia and Finland from the *Pinus sylvestris* (Linn.), or Scotch pine; in Austria and Corsica from *P. laricio* (Poiret); in South Western France from *P. pinaster* (Solander); and in the United States from *P. palustris* (Mill.), the swamp pine and the Loblolly pine, *P. tæda* (Linn.) (Flück. a. Hanb. 604; Bentl. a. Trim. 256–259). Tschirch and Niederstadt (Arch. Pharm. 239, 167), using the method of examination of resins already described, find the oleo-resin from *Pinus sylvestris* contains: *silveolic acid*, 1·5; *silvinolic acids* α- and β-, 58–60; essential oil, 15; *silvoresene*, 20–21; bitter substance, succinic acid, and impurities, 1–2 p.c. (*cf.* Schkatcloff, Chem. Zentr. 1908, i. 2097).

The resin from *Pinus laricio* (Poiret), Austrian turpentine, melts at about 100° and has a yellow colour which on exposure to light becomes red. On boiling with water for a long time and then extracting with ether, caffeic and ferulic acids were obtained and also vanillin (Bamberger, Monatsh. 12, 479). The resin is resolved on digestion with ether into an *α-modification* (80 p.c.), which is soluble in ether, and a *β-modification* (20 p.c.) insoluble in ether. When excess of potash is added to an alcoholic solution of the α-resin or of the crude resin, a colourless crystalline potassium compound is formed which, when treated with hydrochloric acid, gives a powdery precipitate of *pinoresinol*. The caffeic and ferulic acids are in all probability present in an uncombined state (Bamberger, Monatsh. 15, 505). Pinoresinol can be obtained crystalline, m.p. 122°, and has the composition $C_{19}H_{20}O_6$. The β-resin, on purification, forms a chocolate brown powder and appears to have the composition

$$C_{30}H_{30}O_6(OMe)_2$$

Its properties are those of a tannol, whence it is named *pinoresinotannol* (Bamberger and Landsiedl, Monatsh. 18, 481). Tschirch and Schmidt (Arch. Pharm. 241, 570) found 100 parts of the oleo-resin to contain: *laricopinic acid*, 25; *laricopinonic acid*, 34; essential oil, 35; resin, 2; water, bitter substance and impurities, 3–4 parts.

Tschirch and Brüning (Arch. Pharm. 238, 630) find in Bordeaux turpentine, the oleo-resin of *P. pinaster* (Solander), 6–7 p.c. of *pimaric acid* $C_{20}H_{30}O_2$, crystals, m.p. 144°–146°; 48–50 p.c. of α- and *β-pimarolic acids*; 28–30 p.c. of essential oil; 5–6 p.c. of resene; and 1–2 p.c. of succinic acid, alkaloid, colouring matter, water, and impurities. For concreted French turpentine, common frankincense or galipot, *see* RESINS.

Pinus palustris (Mill.) is the 'long leaf pine' of the United States and is the chief source of the turpentine and resin prepared there. In 100 parts of the oleo-resin, there are contained *palabienic acid* $C_{18}H_{20}O_2$, m.p. 110°, 5; *palabietic acid*, $C_{20}H_{30}O_2$, m.p. 153°–154°, 6–7; *palabietinolic acids*, $C_{18}H_{24}O_2$, 53–57; essential oil, 20–22; *paloresene*, 10; bitter substance, impurities, and water, 2–3 parts (Tschirch and Koritschoner, Arch. Pharm. 240, 568).

Canada turpentine, Canada balsam, Balsam of fir. A product of the balsam or balm of Gilead fir, the *Abies balsamea* (Mill.). This is incorrectly called balsam, and it must not be confounded with true balm of Gilead or Mecca balsam (*cf.* Flück. a. Hanb. 612; Bentl. and Trim. 263). A similar turpentine is obtained from the hemlock spruce, *Tsuga canadensis* (Carr.). This has been investigated by Tschirch and Brüning (Arch. Pharm. 238, 487). 100 parts of the turpentine contain *canadic acid* $C_{19}H_{34}O_2$, m.p. 135°–136°, 13; *canadolic acid* $C_{19}H_{28}O_2$, crystalline, m.p. 143°–145°, 0·3;

α- and β-*canadinolic acids*, $C_{19}H_{30}O_2$, m.p. 89°–95°, 48–50; essential oil, 23–24; *canadoresene*, 11–12; succinic acid and impurities, 1–2 parts. The oleo-resin also contains an alkaloid soluble in water. On dry distillation, formic, acetic, and succinic acids are formed.

Venice turpentine, Larch turpentine. The exudate of the larch *Larix decidua* (Mill.), mostly obtained from the Tyrol. Tschirch and Weigel (Arch. Pharm. 238, 387) have isolated *laricinolic acid*, $C_{20}H_{30}O_2$, m.p. 147°–148°, crystals, 4–5 p.c.; α- and β- *larinolic acids*, $C_{18}H_{26}O_2$, which may be identical, 55–60 p.c.; essential oil, 20–22 p.c.; resene, 14–15 p.c.; alkaloid, colouring matter and impurities 2·4 p.c.; succinic acid, 0·1 p.c. (*cf.* Bamberger, Monatsh. 18, 481; Bamberger and Landsiedl, *ibid.* 20, 755).

Strassburg turpentine is the yield of the Silver fir (*Sapin*, Fr.; *Weisstanne* or *Edeltanne*, Ger.), *Abies pectinata* (DC.). The market is supplied chiefly from the Vosges (Fluck. a Hanb. 615; Bentl. a. Trin. 262). In 100 parts the turpentine contains *abienic acid* $C_{13}H_{20}O_2$, m.p. 114°–115°, 8–10; *abietric acid* crystalline, $C_{20}H_{28}O_2$, m.p. 145°–153°, 1·5–2; α- and β-*abietinolic acids*, 46–50; essential oil, 28–31; *abietoresene*, 12–16; alkaloid, colouring matter, water, and impurities, 1–2; succinic acid, 0·05–0·08 parts (Tschirch and Weigel, Arch. Pharm. 238, 411).

Canada balsam from *Abies balsamea* and *A. canadensis* is similar to the last two varieties.

Hungarian turpentine is obtained from the *Pinus pumilio* (Haenke).

Chian turpentine is the turpentine of the older writers, and is derived from a small tree, *Pistacia terebinthus* (Linn.), which inhabits the shores of the Mediterranean and Asia Minor.

Jura turpentine is the product of *Picea excelsa* (Link). The resin melts at about 100°, and when boiled with water gives an aqueous extract which contains *p*-coumaric acid and vanillin (Bamberger, Monatsh. 12, 441). Tschirch and Brüning (Arch. Pharm. 238, 616) isolated *piceapimarinic acid* $C_{20}H_{30}O_2$, crystals, m.p. 144°–145°, 2–3 p.c.; *piceapimaric acid* $C_{13}H_{20}O_2$, 1·5–2 p.c.; α- and β- *piceapimarolic acids* $C_{25}H_{44}O_3$, 48–50 p.c.; essential oil, 32–33 p.c.; *juroresene*, 10–12 p.c.; succinic acid, alkaloid, colouring matter, water, and impurities, 1–2 p.c. (*cf.* Tschirch and Koch, Arch. Pharm. 240, 272).

The resin from *Pinus halepensis* (Mill.) is used in Greece for preserving and flavouring wine. It has been investigated by Tschirch and Schulz (Arch. Pharm. 245, 156).

The resin oil from *Pinus longifolia* (Roxb.), a tree indigenous to the lower Himalayas, forms a white rather tough opaque mass and has a granular structure which is due to the partial crystallisation of the resin acid. The turpentine now largely made from it in Government factories contains l-α-pinene, β-pinene, *d-carene*, $C_{10}H_{16}$, and *d-longifolene*, and $C_{15}H_{24}$ (Simonsen, Trans. Chem. Soc. 1920, 117, 570.)

The resins of the Norway pine, *Pinus resinosa* (Solander) and the Douglas fir, *Pseudotsuga Douglasii* (Carr.), have been investigated by Frankforter (J. Amer. Chem. Soc. 28, 1467; 31, 561). Russian 'white pitch,' which is probably the product of *Abies sibirica* (Ledeb.), or of *Picea obovata* (Ledeb.) has been examined by Tschirch and Koritschoner (Arch. Pharm. 240, 584). Brooks (Philippine J. Sci. 1910, [A] 5, 229) has examined the oleo-resin of *Pinus insularis* (Endl.) and the resinous saps from various pines have been investigated by Schkateloff (Chem. Zentr. 1908, i. 2097).

Tar *v.* TURPENTINE. G. B.

OLEUM. Fuming sulphuric acid (*q.v.*).

OLEUM PIMENTÆ *v.* LAURUS NOBILIS.

OLIBANOLS. Olibanol when isolated from oil of frankincense (*v.* olibanum, art. GUM RESINS) by distillation *in vacuô* has b.p. 117°–119°/22 mm. and yields no pinononic acid when oxidised by cold permanganate. It is called α-olibanol to distinguish it from the isomeride β-olibanol into which it is converted on distillation at atmospheric pressure (b.p. 210°–211°), and which yields pinononic acid on oxidation. α-Olibanol on reduction by sodium and alcohol gives *dihydro-olibanol* $C_{10}H_{18}O$, b.p. 100°–102°/25 mm., which has an odour resembling sage and appears to be an alcohol. It is characterised by a crystalline *o-nitrobenzoate*, m.p. 135°–137°. β-Olibanol does not show these properties. Another isomeride, γ-olibanol, b.p. 114°–116°/15 mm., $d^{18}=0{\cdot}9502$, isolated from a different specimen of oil of frankincense, gives no dihydro compound, and does not yield β-olibanol on distillation (Fromm and Klein, Annalen, 1921, 425, 208).

OLIGOCLASE *v.* FELSPAR.

OLIVE, the fruit of *Olea europæa* (Linn.).

Many varieties are known. The fruit is largely used as a source of olive oil (*v.* OLIVE OIL). It usually consists of about 80 p.c. of flesh and rind, 17·5 p.c. of stone, and 2·5 p.c. of seed. All parts of the fruit contain oil, but the best is obtained from the flesh. According to König, the following gives the average composition of the various parts of the fruit:—

	Water	Protein	Fat	Carbohydrates and fibre	Ash
Flesh .	30·1	5·2	51·9	10·5	2·3
Stone .	9·2	3·5	2·8	83·3	1·1
Seed .	10·6	18·6	31·9	36·7	2·2

whilst the ash has the following percentage composition:—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Flesh	80·9	7·5	7·5	0·2	0·7	1·3	1·1	0·7	0·2
Stone	58·8	6·6	7·5	0·4	0·8	16·7	3·3	1·3	4·7
Seeds	30·3	2·0	30·4	1·2	0·1	28·2	2·4	5·4	0·1

The fruit has an insipid, bitter taste, and is usually pickled before being eaten, salt and spices being used for the purpose. The following are American analyses of the edible portions of pickled olives:—

	Water	Protein	Fat	Carbohydrates and fibre	Ash
Green olives .	58·0	1·1	27·6	11·6	1·7
Ripe olives .	64·7	1·7	25·9	4·3	3·4

Ground olive stones or 'poivrette' have been used to adulterate pepper (*v.* Wynter Blyth, Foods; also Martelli, Staz. Sper. Agrar. 1895, 28, 53). For results of the examination of olive leaves and bark *v.* Canzoneri (Gazz. chim. ital. 1906, 36, [ii.] 372) and Power and Tutin (Chem. Soc. Trans. 1908, 93, 891, 904). According to Bourquelot and Vintilesco (Compt. rend. 1908, 147, 533), olives contain a glucoside—*oleoeuropein*—a yellow powder with bitter taste, hydrolysable by emulsin, which is present in the fruit, leaves, and bark, yielding dextrose (*v.* also Power and Tutin, Pharm. J. 1898, [iv.] 27, 714; and Vanzetti, Atti R. Accad. Lincei, 1909, 18, ii. 188). H. I.

OLIVE OIL. Olive oil is obtained from the fruits of the olive tree, *Olea europæa* (*sativa*), L. The olive tree is probably indigenous to Western Asia, but was at an early date introduced into all the countries bordering on the Mediterranean. More recently the cultivation of the olive has been introduced into California, South Africa, and Australia. The olive tree thrives best in a sub-tropical climate, and its successful cultivation extends in Europe as far north as latitude 44½°. In America it scarcely extends to latitude 34°. Attempts have also been made in several parts of India to cultivate the olive tree, but although it grows well and flowers, the fruit seldom matures.

The olives intended for oil production are gathered just before the period of maturity, as the oil obtained from the barely ripe fruit is much superior in quality to that obtained from fully ripe or over-ripe fruits.

The proportion of oil in the fruit goes on increasing to the maximum found in fruit which has reached complete maturity: it then decreases slowly. The ripe olives contain up to 70 p.c. of oil. This figure is, however, an exceptional one, the fleshy part of the best cultivated olives containing only from 40 to 60 p.c. of oil. The Algerian olives vary in their proportion of oil within wide limits, from 10·03 p.c. to 32·98 p.c. (in the Jemmap olives). The Californian olives also yield much smaller quantities of oil than the best cultivated European varieties.

The technical processes employed for the production of olive oil are still represented by both the oldest and crudest processes (*see* preparation of OILS (FIXED) AND FATS) and by the most modern methods adapted to large-scale working.

The very finest oils are obtained from hand-picked fruits by first crushing them in a mill without breaking the kernels. Exceptionally fine qualities are prepared by peeling hand-picked fruits and pressing lightly, after carefully removing the kernels. The crushed marc is then expressed in a hydraulic press; the oil so obtained ranks as the best edible oil—'*huile vierge*,' '*huile surfine*.' Commercial brands of this quality are 'Provence Oil,' 'Aix Oil,' 'Nice Oil,' 'Var Oil.' The oils sold as 'Finest Tuscan Cream,' 'Riviera Oils' (Genoa), 'Bari Oils,' may also be ranked amongst the best edible oils, although they are distinctly lower in value than the oils of the South of France, and come nearer the following somewhat inferior quality. This is obtained by pouring some cold water on the marc, after the pressure in the hydraulic press has been released, and pressing again. Such inferior oil is also sold as an edible oil, either alone or mixed with the oil of the first expression as '*Salad Oil*,' '*huile fine*,' '*huile de table ordinaire*.'

The pulp left in the press yields, after mixing with hot water and pressing once or twice, a bright oil used for lubricating purposes, as burning oil, and for soapmaking.

In most of the smaller works, the kernels are not removed and are crushed together with the fruit. In large establishments, however, the kernels are removed and crushed separately, yielding olive kernel oil. (*See* tables OILS (FIXED) AND FATS.) The repeatedly pressed pulp ('grignons') still contains a considerable amount of oil, varying from 10 to 22 p.c. This pulp is beaten with hot water in special mills—*moulins de ressence*—resembling edge-runners. The oil cells are thereby further broken up; the ground mass, together with the water, is then allowed to run into a series of vessels, arranged in tiers, where the water separates from the oil and broken cellular tissues. The oil and the tissue rise to the surface, to be skimmed off, whilst the heavier crushed kernels fall to the bottom. The latter are known as '*grignon marc blanc*.' The emulsion of oil and cellular tissue, which has been skimmed off, known as '*grignon marc noir*,' is heated and subjected to a fresh expression in a hydraulic press. The oil so obtained is termed 'huile de ressence,' and the pressed residue is known as 'tourteau de ressence.' The *huile de ressence* is allowed to rest in large tanks at a somewhat elevated temperature, when a clear oil separates on the top—'*huile claire de ressence*'—and a lower layer of thicker oil 'Olive Oil Grease' (*pâte de ressence*) settles out.

In some establishments the marc, instead of being boiled with water, is thrown into pits where the pulp undergoes a kind of fermentation, whereby the oil is set free and gradually rises to the top. Oil of this kind is known as '*huile d'enfer*.' The name 'huile d'enfer' is applied also to oil which has settled out from the waters obtained from the press after moistening and boiling the pulp, which has been stored in underground cisterns ('enfers'). To this class of oil belong the bagassa (bagasse) oils, which are obtained principally in Portugal from fermented marc. These oils contain as much as 60–70 p.c. of free fatty acids.

'Tournant oil' is a commercial product of the quality of the 'huiles d'enfer,' obtained from the fermented marc of expressed olives; it contains a considerable quantity (up to 26 p.c.) of free fatty acids, and therefore forms a very complete emulsion (which constitutes its value) with a solution of sodium carbonate. Such Turkey-red oil was first employed for this purpose by Haussmann, 1792, and then recommended by Koechlin Frères.

The cake remaining after the removal of the *huile de ressence*, termed 'tourteau de ressence,' or 'sanza,' is finally deprived of its last content of oil by extracting with solvents, sometimes after a preliminary drying. The solvent usually employed in France and Italy is carbon disulphide. Hence these oils are termed 'sulphocarbon oils,' 'sulphur olive oils.' They have a deep green colour, due to the chlorophyll which has been extracted by the solvent, and contain the more solid portion of olive oil which has remained behind in the pulp. These oils contain large proportions of free fatty acids as also notable amounts of lactones.

They differ from expressed oils in having a higher sp.gr., lower iodine value (77·5–80·2), a high acetyl value, and lower solidification point of the fatty acids (*e.g.* 17·5–19·7). Such extracted oils not infrequently contain traces of carbon disulphide and of free sulphur. They may be recognised by the method suggested by Milliau of detecting the carbon disulphide. For this purpose a mixture of 50 grms. of the oil, with 10 c.c. of amyl alcohol is distilled, the first 5 c.c. of the distillate collected, and 4 c.c. of this distillate mixed with 1 c.c. of cotton-seed oil and a few mgs. of sulphur, and heated in a sealed tube for an hour. The test is thus the converse of Halphen's test for cotton-seed oil (*q.v.*).

For the physical and chemical characteristics, *see* tables OILS (FIXED) AND FATS.

Some Tunisian olive oils are so rich in glycerides of solid fatty acids that they deposit 'stearine' on standing. Hence they are unsuitable for table oils. Therefore, such Tunisian oils must be 'demargarinated' (*see* OILS (FIXED) AND FATS).

The extracted cake is sold as manure. The press residues which have yielded superior kinds of olive oil, would be suitable for feeding cattle; but as the oil, which can be easily recovered by extraction—about 10 p.c. of the residues—is too valuable, olive cakes are only used locally and to an inconsiderable extent as cattle food.

Olive oil typifies eminently a non-drying oil. On account of its comparatively high price, it is adulterated to an enormous extent. How far the blending of various olive oils of different qualities should be considered as an adulteration must be decided in each given case. Undoubtedly the 'finest Nice oil,' which has been prepared by blending a genuine Nice oil with Tunisian oils or other olive oils, must be considered as of inferior quality. At present, olive oil is most frequently adulterated with tea-seed oil, as the detection of this oil offers greater difficulties to the analyst than those oils which were previously used to a much greater extent, viz. arachis oil, cotton-seed oil, sesamé oil (rape oil). The adulteration with hydrocarbons has practically ceased for the simple reason that they are too easily detected, but during the period of the war substitutes for olive oil composed entirely of purified petroleum oil were extensively sold. J. L.

OLIVENITE. A basic copper arsenate $Cu_3(AsO_4)_2{\cdot}Cu(OH)_2$, crystallised in the orthorhombic system. It forms small crystals of prismatic habit; or more usually globular aggregates of radiating needles, sometimes so fine that the material has a velvety appearance. The characteristic olive-green colour (hence the name) ranges from a dark shade in the crystals to pale or almost white in the finely fibrous masses; the latter variety is known as *wood-copper*. Sp.gr. 4·1–4·2. It was formerly found is some abundance in the upper workings of the copper mines near St. Day in Cornwall, and also in the Tintic district in Utah. In Cornwall it has resulted from the alteration of copper-pyrites and mispickel, while in Utah the mother mineral was enargite (Cu_3AsS_4). The arsenic is sometimes partly replaced by phosphorus, forming a passage to the isomorphous and very similar mineral *libethenite* ($Cu_3(PO_4)_2{\cdot}Cu(OH)_2$) originally found at Libethen in Hungary.

L. J. S.

OLIVER'S BARK. The dried bark of *Cinnamomum Oliveri* (Bailey).

OLIVINE. An abundant rock-forming mineral consisting of magnesium orthosilicate with variable amounts of ferrous orthosilicate $(Mg,Fe)_2SiO_4$, crystallised in the orthorhombic system. The member at the magnesium end of this isomorphous series is known as *forsterite* (Mg_2SiO_4), and that at the iron end is called *fayalite* (Fe_2SiO_4). The latter is a common constituent of crystalline iron slags. Distinctly formed crystals of olivine are of rare occurrence; granular masses are more common. The colour ranges from pale yellowish-green to brown, depending on the amount of iron present. The mineral is decomposed by hot hydrochloric acid with separation of gelatinous silica. It occurs in many basic and ultra-basic rocks of igneous origin (basalt, gabbro, peridotite, etc.), and it is an important constituent of stony meteorites. Deposits of diamond, platinum, chromite, and nickel-ores are usually associated with olivine-rocks, and by the weathering of these rocks, serpentine and associated deposits of serpentine-asbestos (chrysotile), steatite, magnesite, and meerschaum are formed. The only direct practical application of olivine is as a gemstone; the clear, transparent stones are yellowish-green (*chrysolite*) or rich olive-green (*peridot*) in colour. Sp.gr. 3·3–3·37, H 6½, FeO about 9 p.c. for gem-varieties. Such material comes mainly from the island of St. John in the Red Sea, and it is also collected from ant-hills in Arizona and New Mexico. L. J. S.

OMEIRE. A drink resembling koumiss, prepared by the natives in South-West Africa by filling gourd bottles, which contain some fermented milk, with milk, shaking well and allowing to stand. It is a thick, semi-coagulated liquid, possessing a pleasant wine-like smell, and a slightly sour taste; it contains a little alcohol (Arch. Pharm. 1887, 744).

OMNOPON. Trade name for a mixture of the soluble hydrochlorides of opium alkaloids.

OMOROL *v.* SYNTHETIC DRUGS.

ONION SKINS. The outer dry skins of the bulb of the onion, *Allium cepa* (Linn.), were formerly employed for dyeing purposes. According to Leuchs (Farben und Färbekunde, 1825, 1, 434), 'the outer skins of onion bulbs which are of a brownish-orange colour have long been used in Germany for dyeing Easter eggs yellow, and in conjunction with alum for dyeing woollen, linen, and cotton materials. The colour is fast and particularly brilliant. From Kurrer's observations onion skins are very suitable for dyeing cotton, on which they give a cinnamon-brown with acetate of alumina, a fawn with alumina and iron, a grey with iron salts, and a variety of shades with other additions.'

The colouring matter was extracted by boiling the skins with distilled water for one hour, and the yellow extract on keeping gradually deposited the impure dye as a pale olive precipitate. The average yield was 1·3 p.c. This was extracted with alcohol, the concentrated extract treated with ether and the ethereal solution washed, until a tarry precipitate no longer separated. On extracting the ethereal solution with dilute alkali the whole of the colouring matter was removed, and on neutralising the alkaline liquid a yellow precipitate was thrown down, which was purified by crystallisation from dilute alcohol. The acetyl compound melted at 190°–191°, and there could be no doubt as to the identity of this colouring matter with *quercetin* (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1295). Attempts to isolate a quercetin glucoside from onion skins have hitherto failed, and it seems that such a compound is absent, at least in the outer dry material. A. G. P.

ONOFRITE. Sulphide and selenide of mercury Hg(S,Se), containing Se 4·6–8·4 p.c. It is found only massive, but is probably isomorphous with the cubic minerals metacinnabarite (HgS) and tiemannite (HgSe). Black granular material has been found at San Onofre in Mexico, Tilkerode in the Harz, Marysvale in Utah, the Black Hills in South Dakota, and the Wan-shan-chang mercury mines in prov. Kwei-chou, Central China. L. J. S.

ONONIS ROOT. Contains a glucoside *ononin* $C_{25}H_{26}O_{11}$, forming colourless needles, m.p. 210°, decomposed by dilute acids into dextrose and *ononetin* (*v.* Hemmelmayr, Monatsh. 1902, 133; 1903, 132).

ONOSMA ECHOIDES. *Onosma echoides* is a biennial plant frequent throughout the Western Himalaya from Kashmir to Kumaon. It is widely distributed from Siberia and Carbut to France (Watt's Dictionary of Economic Products of India, 1891, 5, 487). The roots are violet coloured and yield a dye which is readily extracted by alcohol, giving a red solution, but this is very sparingly soluble in water. In various districts of India it is employed for dyeing wool, and on account of its solubility in oils and fats, to which it imparts a red colour, is also used as a substitute for alkanet. According to Watt (*l.c.*) the bruised root is employed medicinally as also are the leaves and flowers of this plant.

The general properties and colour reactions of the dye present in the root are very similar to those given by alkanet, and there can be little doubt that it contains either the same or closely allied colouring matters. A. G. P.

ONYX. A variety of chalcedonic silica differing from agate only in the straightness and parallelism of its differently-coloured layers, and so suitable for engraving as cameos. The alternate bands of colour are usually white and black, or white and red; in sardonyx they are white and brown. Most of the onyx with intense differences in colour, as now placed on the market, has been coloured artificially by chemical means (*v.* AGATE). L. J. S.

ONYX-MARBLE. Algerian onyx, Mexican onyx, or 'Oriental alabaster' (also called 'onyx' in ancient times and in the marble trade of the present day). A banded, translucent variety of fibrous or granular calcite, or marble, susceptible of a fine polish, and much used, both in ancient and modern times, as an ornamental stone. The coloration, which is distributed in bands or cloudy patches, is due to the presence of ferrous carbonate and ferric hydroxides, and to a less degree of manganese oxides and organic matter. For example, a green marble from Arizona contained 4·27 p.c. $FeCO_3$, and in its brownish-red (oxidised) portions 1·22 p.c. $FeCO_3$ with 3·53 p.c. Fe_2O_3. The percentage of calcium carbonate rarely falls below 90. Onyx-marble is quarried in Algeria, Mexico, and Arizona. (*See* G. P. Merrill, The Onyx Marbles: their Origin, Composition, and Uses, both Ancient and Modern, Rep. U.S. Nat. Mus. for 1893, 1895, 539; G. P. Merrill, Stones for Building and Decoration, 3rd edit., New York, 1903.) L. J. S.

OOLITE (from ὠόν, egg, and λίθος, stone) or *Roe-stone* (Ger. *Rogenstein*). Material showing oolitic structure consists of an aggregate of small (usually less than 1 mm. diameter) spheroidal grains, which may be loose or more often cemented together by the same kind of substance of which the grains themselves are composed. The grains are usually built up of concentric layers around a central nucleus of foreign material; but sometimes they show an internal radiating crystalline structure. Such an oolitic structure is met with in a variety of minerals and rocks, but more particularly in limestone (*q.v.*); and for this reason the term oolite is often limited to an oolitic limestone. By geologists it is applied, not only to such limestones, but also to the whole series of beds forming the upper part, above the Lias, of the Jurassic system, it being here that oolitic limestones are typically developed. Examples are the well-known building stones (freestones) such as the Bath oolite and the Portland oolite. All limestones of the oolitic period do not, however, necessarily show an oolitic structure. The Oolitic strata also include clays (*e.g.* the Oxford clay), whilst in Yorkshire they are represented mainly by sandstones and shales. Oolitic limestones are, further, not confined to this system, but are met with in sedimentary strata of all geological periods, *e.g.* in the Carboniferous Limestone of the Bristol district. At the present time they are forming in the lagoons of coral islands, and an oolitic calcareous sand is found on the shores of the Great Salt Lake in Utah. The calcareous material of the oolitic grains in limestones consists of the mineral calcite. In a few instances, however, it is aragonite, as in the material (Sprudelstein) now being deposited by the hot springs at Carlsbad in Bohemia. Other minerals which sometimes exhibit an oolitic structure are: quartz, *e.g.* from Center Co., Pennsylvania; colourless opal (hyalite) deposited by the hot springs of Tateyama, Japan (K. Jimbō, Beiträge Min. Japan, 1905, 1, 11); and various iron-ores. Amongst the last-named are the carbonate chalybite (*e.g.* the iron-ores of the Cleveland district in Yorkshire), the oxides hæmatite (*e.g.* the Clinton ores of the United States) and magnetite (*e.g.* at Rosedale in Cleveland), the hydroxide limonite (*e.g.* the 'minettes' of Lorraine), and the hydrated silicates chamosite from Chamosen in Wallis, berthierine from Hayange in Lorraine, bavalite from Brittany, greenalite from Mesabi in Minnesota, and glauconite. In some of these cases the oolitic structure no doubt represents that of the limestones which have been replaced metasomatically by the iron-ore.

A structure of the same kind as oolitic structure, but in which the grains are larger (about the size of a pea) is known as pisolitic. The name *pisolite* (from πίσος, pease, and λίθος, stone), or *pea-stone* (Ger. Erbsenstein), is applied to certain limestones, and also to the globular aragonite from Carlsbad in Bohemia. L. J. S.

OOPHORIN *v.* SYNTHETIC DRUGS.

OPAL. Colloidal silica, occurring native in botryoidal and stalactitic forms, or as irregular masses occupying cracks and cavities in certain rocks. It is softer and less dense than quartz; its hardness being only 5½ to 6½, while its sp.gr. varies with the impurities present from 1·9 to 2·3, and for the purer forms 2·1–2·2. Being non-crystalline it should exhibit single refraction, but many varieties, especially of noble opal, are strongly birefringent; the anomaly being probably due to the strain set up by unequal contraction in different directions during the solidification of the gelatinous mass. Opaline silica is nearly always hydrated, but the proportion of water varies from about 2·5 to upwards of 10 p.c. The substance is almost wholly soluble in a hot solution of potassium hydroxide.

The purest opal, known as *hyalite* or *water-opal*, occurs as colourless, transparent masses, resembling glass. *Semi-opal* is a name applied to the dull, opaque varieties, generally more or less impure. *Menilite* or *liver-opal* is a brown opaque mineral, occurring as nodules in the Tertiary strata of the Paris basin, especially at Menilmontant. *Wood-opal* is simply wood fossilised with opaline silica, and retaining the ligneous structure, which produces a pleasing effect when the substance is cut and polished; hence it is used in slabs as an ornamental stone. *Hydrophane* is an opal, which when dry is opaque and dead white, but absorbs water rapidly when moistened, becoming transparent and sometimes exhibiting a play of colours. A fine variety found in Colorado has been brought into use under the name of 'magic stone.' *Common opal* is a general term for any opal which does not display sufficient colour to recommend its employment for decorative purposes. According to its appearance it often receives trivial names, such as *milk-opal*, *wax-opal*, &c. *Fire-opal*, found chiefly in Mexico, exhibits a brilliant hyacinthine or orange colour, which renders it of some value in jewellery. But the finest variety is the *precious* or *noble opal*, a substance which is unique in exhibiting by reflected light a vivid play of iridescent colours. The cause of this phenomenon has been studied by Brewster, Crookes, Behrens, Lord Rayleigh, and others. By most authorities it has been referred to the presence of numerous microscopic pores, fissures, or striæ in the interior of the stone; but Behrens considers it due to the interposition of thin lamellæ of opaline matter having a different index of refraction from that of the matrix (Sitz.-Ber. Akad. Wiss. Wien, Math.-naturw. Cl. 1871, 61, 519). If the colours proceed from distinct patches, like a brilliant mosaic, the stone is termed in trade *harlequin opal*. Precious opal is a mineral of very limited distribution. The oldest mines are those on the Dubnik Hill, near the village of Czerwenitza (Hungarian, Vörösvágás), near Eperjes in Czechoslovakia, where the opal occurs in a matrix of andesite. Slabs of matrix, or 'mother-of-opal,' enclosing brilliant particles of the gem, are polished as ornamental stones. Opal is also found at Gracias-á-Dios, in Honduras; at Queretaro, in Mexico; near the Barcoo river, and several other spots in southern and central Queensland; and at White Cliffs and other districts in northern New South Wales. The Queensland opal occurs in cracks in nodules of jaspery brown iron-ore, and is remarkable for its brilliant blue and green colours; that of White Cliffs, discovered in 1889, occurs in a white sandstone of Cretaceous age. Opals are usually cut *en cabochon*, *i.e.* with a convex surface, but the Queensland stone, occurring in thin layers, lends itself to cameo-work, the brown ferruginous matrix forming an effective background. 'Black opal,' enclosing patches of manganese oxide and exhibiting a brilliant play of colours, has recently been found at Lightning Ridge in northern New South Wales.

In addition to the compact forms of opal mentioned above, there are also loose and friable forms of opaline silica represented by silicious sinter or geyserite (*q.v.*) (deposited by the hot springs of Iceland, New Zealand, and the Yellowstone Park in Wyoming) and by diatomaceous earth or diatomite (*q.v.*) (consisting of the silicious skeletons of diatoms and radiolaria)

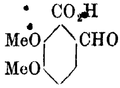
L. J. S.

OPHICALCITE *v.* MARBLE.

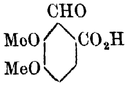
OPHIOTOXIN *v.* SNAKE VENOM.

OPIANIC ACIDS (*dimethoxy-o-aldehydrobenzoic acids*). Three isomerides are known:—

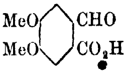
Opianic acid (m.p. 150°) from narcotine—



ψ-Opianic acid (m.p. 121°) from berberine



m-Opianic acid (m.p. 185°) from cryptopine



m-Opianic acid has been synthetically prepared from 4:5-dimethoxyphthalonic acid (1) by boiling with a solution of sodium hydrogen sulphite, or (2) by digesting anilino-*m*-opianic acid with dilute hydrochloric acid (Fargher and W. H. Perkin, Chem. Soc. Trans. 1921, 119, 1724).

OPIAURIN. Opianic acid and phenol, when heated together with strong sulphuric acid, give rise to an intense yellow-red dye. The reaction takes place between the aldehyde group of the acid and the phenol

$$C_6H_2(OCH_3)(CO_2H)(CHO)+2C_6H_5{\cdot}OH$$
$$=H_2O+C_6H_2(OCH_3)_2{\cdot}(CO_2H){\cdot}CH(C_6H_4OH)_2$$

This compound *leucopiaurin* is oxidised during the process to opiaurin $C_{22}H_{18}O_6$. The best results are obtained by stirring an intimate mixture of opianic acid and phenol into sulphuric acid (60°Bé.), and keeping the mixture well cooled. After 24 hours it is thrown into a large quantity of cold water, and the precipitate, when washed and dried, freed from tarry matters by extraction with hot benzene. Opiaurin is soluble in alcohol, ether, and glacial acetic acid, insoluble in benzene and light petroleum. It can only be obtained in the amorphous condition. It dissolves in alkalis with a purple colour; the solution in alcoholic ammonia becomes brownish-yellow on heating, but the purple colour returns on cooling. Sulphurous acid does not reduce it. Opianic acid reacts in a similar way with other phenols, and the reaction can be used to detect the presence of opianic acid, as also of an aldehyde group in aromatic compounds; the reagents are separately dissolved in an excess of cold sulphuric acid; on mixing the solutions the coloration takes place at once (C. Liebermann and P. Seidler, Ber. 20, 873; J. Soc. Chem. Ind. 6, 541).

OPIUM.

Origin.—Opium is the milky juice of the unripe capsules of *Papaver somniferum* (Linn.) or opium poppy, obtained by incision and inspissated by spontaneous evaporation. The plant (*v.* Bentl. a. Trim. 18) is perhaps indigenous to Asia Minor and neighbouring districts of South-Eastern Europe and Western Asia; but it is now cultivated more or less throughout all temperate and sub-tropical countries. It exhibits, however, morphological differences. The two most important varieties which, according to Boissier, are cultivated for the production of opium, are *glabrum*, with subglobular capsules and ten to twelve stigmata, and *album*, with egg-shaped capsules and without apertures (Flora Orientalis, 1867, 1, 116). The former is grown in Asia Minor and Egypt, and the latter in Persia and India. But besides these varieties there are minor distinctions, the petals in the same variety differ in colour, and may be white, red, or violet, with a dark-purplish spot at the base in most cases. The seeds are white or dark-coloured, and contain from a third to half of their weight of fixed oil. The capsules are provided with a lacticiferous system from which the juice exudes when they are incised. This milky juice is present in the plant in all countries where it has been grown, and opium may be collected provided that the rainfall is not too great and the temperature neither arctic nor entirely tropical. That its production is confined for the most part to Asia Minor, Persia, India, and China, is determined by other considerations such as the value of land and the cost of labour.

History.—The drug was known early in the third century B.C. to Theophrastus. Scribonius Largus, in the first century A.D., describes the method of preparing it and remarks that it should only be made from the capsules; for, as Dioscorides, writing a little later, points out, two sorts of opium were in use at that period. One of these, the opium proper, was prepared from the capsules, and the other, 'meconium,' was extracted from the entire plant by means of a solvent. Similar accounts may be found in the works of Pliny and other Latin writers. The opium of the classical period, and indeed the only variety known till the twelfth century, was exclusively that of Asia Minor. The nations of the East appear to have learned of opium from the Arabians, and it seems probable that the use of the drug was favoured by the Mahomedan prohibition of alcohol. They are supposed to have introduced the drug into China in the ninth century. Egyptian opium, 'Opium Thebaicum,' is mentioned by Simon Januensis about the end of the thirteenth century. At this time, and three centuries later, according to Prosper Alpinus, meconium was still prepared in the Thebaïd in Upper Egypt.

In India opium was collected early in the sixteenth century. Barbosa describes a variety produced in Cambay. Pyres, the first European ambassador to China, writing in 1516, mentions three varieties of opium, obtained respectively from Egypt, Cambay, and from the kingdom of Coûs. The last-mentioned district is Kus Behár, south-west of Bhotan in Bengal. Garcia d'Orta, a little later, remarks that Cambay opium is chiefly derived from Malwa. The opium production was a State monopoly in India under the Moguls, and after the victory of Clive at Plassy in 1757 the monopoly passed into the hands of the East India Company. The manufacture then greatly increased, and it has gone on increasing until within the last few years. It was during the seventeenth century that the first accounts reached us of the production of opium in Persia. Kämpfer found that the 'theriaka,' which had long been held in high esteem by neighbouring nations, was made by mixing the finer sorts of opium with spices.

The Chinese obtained their opium from India. Until the beginning of the eighteenth century it formed part of the return cargo of their junks. The importation was then small, and it was used almost exclusively in medicine as a remedy for dysentery. The imports did not reach 1,000 chests (Malwa chests contain one pecul, or 133⅓ lbs., Patna chests 160 lbs.) until 1767, when the trade was mostly in the hands of the Portuguese. In 1790, under the East India Company, it had become 4054 chests. It was at this time that the habit of smoking began to spread in China. To promote the trade the East India Company established an opium depôt of two ships, which lay off the island of Macao, at the entrance to the Canton river. The importation went on increasing, notwithstanding that it was forbidden by the Chinese Government in 1796, and that an edict was issued in 1820 prohibiting opium-laden ships from entering the river. The trade, which between 1820 and 1830 had risen to 17,000 chests annually, then assumed a contraband character. Complaints, however, continued, and when in 1839 it was decided to enforce the law, this, together with other difficulties, led to a war with England which terminated in the treaty of Nanking in 1842. By this treaty five ports were opened to foreign trade, and the island of Hong Kong was ceded to the British Government. The export of opium from India into China, which in 1870 amounted to 55,000 chests, increased to 95,000 chests in 1880. Owing to Chinese home production, however, the importation of Indian opium then began to decrease until in 1890 it fell to 70,000 chests and in 1907 to 50,000. Recently, an important movement has arisen in China to put a stop to opium smoking throughout the Empire, and to this end gradually to terminate both the home production of the drug and its importation from India. With regard to the Indian importation, the wish of China has been met by the Government of this country, and notwithstanding the serious loss which it entails to the revenue of India, which in 1880 amounted to Rs.8,500,000, and to the Indian poppy cultivators, the British Government, reciprocating the views expressed by the Chinese, entered into an agreement, the effect of which has been that the Indian exportation to China came to an end in 1913.

Numerous attempts had been made during

the seventeenth and eighteenth centuries to prepare active condensed extractives from opium, but no constituent of a definite nature was discovered until the beginning of the present century. Derosne in 1803 noticed a separation of crystals on diluting an aqueous extract of opium (Ann. Chim. [i.] 45, 257). Their basic character was demonstrated by Robiquet in 1817 (*ibid.* [ii.] 5, 275), and the compound is now called *narcotine*. Derosne noticed that opium solutions are precipitated by alkalis, but thought that the precipitate was the same compound which he had previously isolated. Seguin in 1814 described what was probably the chief active constituent of opium (*ibid.* [i.] 92, 225), but to isolate in a definite form and make known the basic properties of *morphine* was reserved for Setürner, an apothecary of Eimbeck in Hanover, whose work extended from 1805 to 1816. During the same inquiry, in 1806, Setürner also brought to light *meconic acid*, with which the morphine is combined. Morphine was the first compound known belonging to the class of vegetable bases, which has since become so important; for although narcotine was isolated just before, its properties as an alkaloid were not ascertained until afterwards. Further historical and other details will be found in the article on opium in ‘Pharmacographia’ (Fluck. a. Hanb. 272), from which many of the facts given have been obtained.

Production.—Asia Minor.—Opium is collected in Asia Minor for the most part by small peasant proprietors, the largest quantity being obtained in those countries lying to the west, and having Smyrna and Constantinople for their ports of shipment. The product of these countries is the *Turkey* opium of English commerce, and of all available varieties it is the richest in morphine. The poppy grown is the variety *glabrum* of Boissier. The flowers are purplish or sometimes white, and the seeds white to deep violet. The plant grows in elevated as well as lower situations, and requires a moist soil and much attention and skill on the part of the cultivator. Details of the mode of preparing the soil and management of the crop are given by Maltass (Pharm. J. [i.] 14, 395) and Heffler (*ibid.* [ii.] 10, 434), and in the official directions drawn up by the Turkish Government for the promotion of the opium culture in Macedonia (*ibid.* [iii.] 13, 918). The crop is sometimes destroyed by early frosts, drought, or the attack of locusts. The seed is sown from November to March, and the flowering takes place from May to July. In this way successive crops of capsules become ready for incision during a period of about three months, and a saving in the cost of labour is effected.

In the course of a few days, after the petals have fallen, when the capsules are some 1½ inches in diameter, they are ready for incision. This is done transversely around the middle by means of a knife. The operation is one requiring skill, for if the incision be not deep enough an incomplete flow of juice results, and if it be too deep some of the juice is lost inside the capsule. The incisions are made in the afternoon, and the exuded and partly hardened juice is collected the following morning. It is scraped off and placed on a poppy leaf. Masses of hardened juice thus obtained are allowed to stand in the shade to dry still further, and are then made into lumps of varying size and sold to dealers in the towns. By these the opium is manipulated into cakes suitable for the market, enveloped in poppy leaves and packed in bags, into which Rumex fruits are thrown to prevent the cake adhering together. The bags are then sealed and transmitted to Smyrna and Constantinople, where they are opened in presence of the seller, the buyer, and a public examiner. The examiner scrutinises the drug piece by piece, and by its physical characters classifies it as (1) *prime*, (2) *current*, and (3) *chiqinti*. The ‘current’ constitutes the great bulk of mercantile opium. An important addition to the profits of the opium culture is the sale of poppy seed, from which the oil is expressed and used for a variety of purposes. It is a bland, limpid, drying oil, of a pale colour (Maltass; Heffler; Scherzer, Pharm. J. [iii.] 11, 835).

Turkey opium, as it appears in English commerce, consists of rounded masses, generally from ½ to 2 lbs. in weight but sometimes larger or smaller. Externally it is covered with poppy leaves and Rumex ‘chaff.’ It has a bitter taste, and peculiar, though not altogether disagreeable, odour. The following are among the more important districts, the products of which come to Constantinople: Bogaditz; Kara-hissar-Sahib; Kutchaya; Balukhissar; Kurkagatsch; Ismid or Ghéve, the product of Geiveh; Beybazar; Angora; Malatia; and Tokat. In addition to these the Constantinople market receives the opium of Macedonia and, until recently at least, small supplies from Bulgaria. The cultivation of opium in Macedonia commenced in 1865 from seeds brought from Karahissar. In 1882 the districts of Kotchava, Straumnitza, and Tikvish exported 135,000 lbs. by way of Salonica, whence it is termed collectively Salonica opium. The opium districts in Bulgaria are Kustendil, Lowtscha, and Halitz. The produce is mostly consumed by local pharmacy; but, while the country remained under Turkish dominion, any surplus found its way to Constantinople.

The market at Smyrna receives the products of Afium Karahissar, Ushak, Akhissar, Tanshauli, Isbarta, Koniyeh, Bulladan, Hamid, Magnesia, and that collected in the neighbourhood which is known as Yerli.

In the English market, Turkey opium is divided into three classes, known as ‘shipping,’ ‘druggists’,’ and ‘manufacturing’ opium. As *shipping* opium are classed those varieties which contain the least proportion insoluble in water, and which yield the greatest quantity of extract adapted for smoking. These are the opiums of Malatia, Tokat, Salonica, Balukhissar, Kurkagatsch, Bokaditz, and ‘prime’ Angora and Yerli. This opium is exported to China, Peru, the West Indies, British Guiana, Brazil, and for reshipment, to the United States. *Druggists’* opium is selected for a high percentage of morphine and includes the varieties which are used in medicine. It has a firmer consistence and a darker colour than the others. In England the products generally chosen are: Beybazar, Yerli, Karahissar, including Adet, Amasia, Akhissar, and ‘current’ Smyrna and Angora; for America, Ushak, Yerli, and Karahissar; and for the Continent, Ghéve. All these varieties have been used for the preparation of alkaloids, the deciding factor being market price.

Good Turkey opium contains, when dry, upwards of 12 p.c. of morphine. If less than 10 p.c. is found in a specimen adulteration may be suspected. The following are typical results obtained in recent years by the method of assay official in the British Pharmacopœia: Malatia 11·0–11·76 p.c., Tokat 11·5–13·4 p.c., Hadji Keni 11·5 p.c., Druggists' 11·0–12·6 p.c., Marmora 10·3 p.c., Tikvish 13·4 p.c., Kumanova 13·4 p.c., Keuprulu 14·3 p.c., Ichtib 13·4 p.c., Straumnitza 13·1 p.c.—all in the normal moist condition; the moisture varied from 25 to 35 p.c. The opium used in medicine in the British Empire is required when dried to contain not less than 9·5 nor more than 10·5 p.c. of anhydrous morphine, unless used as a source of Tincture or Extract of Opium, when it may contain, after drying, not less than 7·5 p.c. (Brit. Pharm. 1914), while the official requirement in the United States of America is that the opium in its normal, moist condition, should yield not less than 9·5 p.c. of anhydrous morphine, but 'opium granulation' must yield not less than 10 p.c. nor more than 10·5 p.c. of anhydrous morphine (U.S. Pharm. ix.).

Among the various adulterants which have been detected, from time to time, in Turkey opium are: sand, clay, grape-juice thickened with flour, fig-paste, liquorice, half-dried apricots, tragacanth, pounded poppy capsules, and even turpentine, stones, and bits of lead.

Egypt.—Only a small quantity of opium is now exported from Egypt. Owing to its inferior quality it is not regularly imported into England. Small consignments are, however, sent to Turkey and other countries on the Mediterranean sea-board. It is cultivated in Upper Egypt near Esneh, Kenneh, and Assiout, the ancient Thebaid. Allen, in 1861, describes the collection of opium from a white poppy The capsules are slit twice transversely, and the juice collected the following day with a sort of scoop-knife, and placed on a leaf, in the sun, to harden (Pharm. J. [ii.] 4, 199). The product is sent out in cakes, enveloped in poppy leaves, but without Rumex fruits. According to information supplied to Martindale, the best opium is collected at Akmim, on the right bank of the Nile, 320 miles above Cairo; while at Assiout, 250 miles above, an inferior quality is produced. A piece of Akmim opium, in the form of a hard flat cake, four inches in diameter, and one inch in thickness, contained 7·24 p.c. of morphine. There was the mark of a leaf adhering to it, and it had a rough and irregular appearance. A specimen from Assiout, consisting of segments of a cake, much softer and evidently adulterated, yielded only 0·6 p c of morphine (Pharm. J. [iii.] 19, 743). Other specimens have given 5·8–12·2 p.c. (Guibourt, J. 1862, 374), 3·4–3·9 p.c. (Petermann, J. 1866, 704), and 5·8 p.c., together with 8·7 p.c. of narcotine (Flück. a. Hanb.). It has also been shown by Gastinel that opium can be made in Egypt containing 11–12 p.c. of morphine. The fact that it generally contains only half that proportion is due partly to an over-moist soil and unskilful collection, but also doubtless to adulteration (Flück. a. Hanb.).

Persia.—The quantity of opium produced in Persia has until recent years been small and inferior in quality. The strongest, the *Teriak-e-Arabistani*, was obtained from Dizful and Shuster, in Khuzistan. A good quality was produced near Sari and Balfarush, in Mazandaran, near the Caspian, and in the southern province of Kerman. Inferior sorts came from Shahabdul-azim, Kashan, and Kum. The cultivation extends into Turkestan, where a sort of meconium is also manufactured. Part of these products went overland to China, by way of Bokhara, Khokan, and Kashgar, and another part found its way to Constantinople, by way of Trebizond, to be sold as Turkey opium (Flück. a. Hanb.). More attention is, however, now given to the cultivation of the plant and the collection of the juice, and there is less adulteration, the result being a great increase in the trade. The poppy cultivated is the variety *album* (Boissier), having roundish ovate capsules. Shiraz and Behbahan. the latter in the neighbourhood of Bushire, and other new districts, furnish supplies (Pharm. J. [iii.] 11, 804), and old centres like Kum, Teheran, and Yezd, have improved the quality of their product (*ibid.* [iii.] 15, 113, 438). Ispahan has now become the chief centre of the opium cultivation, the other important districts being Shiraz, Yezd, Khonsar, and also Khorasan, Kermanshah, and Fars.

About the year 1870 a regular export trade of Persian opium was established by water from the ports of Bushire and Bunder Abbas, in the Persian Gulf, and the quantity exported increased rapidly. By far the greater part is now shipped from these ports direct to Hong Kong, where it competes in the market with the product of Patna, Benares, and Malwa. A smaller part is shipped to the Straits Settlements, and the rest to England. A less important trade continues with Constantinople, by way of Trebizond and Samsun, and part of the opium made in Teheran, Tabriz, and Kermanshah, also finds its way to Smyrna.

In China, Persian opium has, to a certain extent, replaced Indian opium owing to its being manufactured to suit the Chinese taste. After it has been once smoked the residue in the pipes, if the opium is of good quality, can be used mixed with fresh opium some six or seven times, whereas Benares opium cannot be used thus more than once. The smoke of the Persian opium is milder and in consequence more suitable to a tropical climate (J. Soc. Chem. Ind. 1892, 646).

The greatly increased consumption of opium in Persia has led to the extension of the cultivation of the poppy over the whole country. The capsules are ready for cutting at the beginning of June. Since the lightest coloured opium commands the best price in the market, the incisions in the poppy heads are made at sunset and the exuded sap is collected before sunrise, as sunlight discolours the product. Vertical incisions are made, and the juice is collected and conveyed to the market in copper vessels. There it is manipulated to suit the tastes of buyers in Hong Kong and London, whither it is exported between September and January. One of the most celebrated products is that of the village of Kupa, a short distance east of Ispahan.

The opium for home consumption in Persia is prepared by adding 20 p.c. of foreign matter to the crude opium after its volume has been reduced one-sixth by evaporation. The added material is usually 'sarcocolla,' the resin of *Penæa mucronata* (Linn.), but sometimes a boiled extract of dried poppy heads, the seed of wild rue, and an extract obtained by steeping fresh poppy leaves in water, are added. The mixture is then boiled slowly for 3 hours with constant stirring, and the paste thus obtained is kneaded and rolled into small sticks for the market. The opium left in the pipes after smoking is prepared for further consumption by being mixed with about 10 p.c. of raw opium and is then smoked as *Teriak-suchte* (burnt opium) or is eaten in the form of pills. The opium for export which is sold in lumps is prepared from the raw opium by drying until its bulk is reduced by about a quarter, and then adding from 50–70 p.c. of grape juice or other unknown ingredients. This opium is homogeneous and it does not present a granular appearance like the Turkish opium; it is also remarkably uniform in moisture content, averaging about 10 p.c. Assays of a large number of samples conducted according to the method of the British Pharmacopœia during the past ten years show from 9–12 p.c. of anhydrous morphine, with an average of 10·3 p.c.

India.—Opium is one of the most important products of India. It is a State monopoly of the Bengal Government in Behar and Benares, and is cultivated free in the Malwa and other districts of the native States, whence on arrival in British territory it pays duty.

Some years ago, large quantities of Indian opium were regularly exported to China. Towards the close of 1906, however, the Chinese Government ordered that within ten years the growth and consumption of opium in China must be suppressed. In 1907, an agreement was concluded whereby the amount exported to China from India should be reduced annually, and in 1913 the sale of opium to China was brought to an end (Bull. Imper. Inst. 1915, 507).

The area devoted to poppy cultivation in Bengal comprises the large central tract of the Ganges, about six hundred miles in length and two hundred in breadth. It extends east and west, from Dinajpur to Agra, and north and south, from Gorakhpur to Hazaribagh. According to Watt, the average annual area actually occupied by the poppy in Bengal for the last thirty years has been 490,000 acres, but in consequence of the cessation of export to China the total area in India has gradually decreased from 769,000 acres in 1903–4 to about 241,000 acres in 1912–13 (*l.c.*). The State does not restrict the cultivation of opium; but it is a monopoly in the sense that what is cultivated must be sold to the Government at a price agreed upon beforehand. One object of these regulations is to prevent the neglect of cereals, for the poppy culture is very much more profitable; in Malwa it is said to realise from three to seven times as much as the ordinary crops. The opium of Behar and Benares is sold at auction in Calcutta, part is retained for consumption in India, the rest being available for export to this and other countries.

The remainder of the opium raised in India is produced by the native States. The most important centre is the broad tableland of the Malwa and the adjoining slopes of the Vindhya Hills. The opening of the railway has given a great impetus to the cultivation in Rajputana and Malwa. Smaller quantities are produced in the Punjab, not only in the plains, but to the eastward of Lahore, in the valley of Bias, as high as 7500 feet above the sea. Kulu also produces excellent opium. It is raised in Nepal, Basahir, and Rampur, and at Doda Kashtwar, at the base of the Himalayas, in the Jammu territory (Flück. a. Hanb.). Nearly all the opium produced in the native States, however, enters British territory, and pays a duty according as it comes from the districts of Ahmedabad, Ajmere, or Malwa. It is then sent to Bombay, whence it is shipped under the general name of Malwa opium.

The poppy grown in India is of two varieties: Bengal opium being derived mainly from white-flowered races, while Malwa opium is largely obtained from plants with purple flowers (Bull. Imper. Inst. 1915). In addition to the dangers to which the crop is exposed in Asia Minor the plant in India is liable to the attack of a parasitical species of broom rape, *Orobanche indica*, which attaches itself to the roots and causes the plant to wither. The factory for the Behar district is at Patna, and for the Benares district at Ghazipur, where the Government agents are stationed. In Benares and Behar the seed is sown in November, and the capsules are ready in February or March. They are then incised or scarified vertically, by means of an instrument called a 'nushtur,' constructed of several blades bound together (*cf.* plate, Pharm. J. [i.] 11, 207). This operation is repeated, in the course of a few days, on different sides, each capsule being scarified from two to six times. The next morning the juice, which has exuded, is scraped off by the use of a sort of concave trowel made of sheet iron, called a 'seetoah,' and collected in earthen pots. The poppy capsules are afterwards utilised in a variety of ways and the oil expressed from the seeds. In Malwa the capsules are ready in March or April. A somewhat different instrument is used to collect the juice, and from time to time this is dipped in linseed oil to prevent the juice adhering. Owing to the heavy dews the juice in India is much more moist than in Asia Minor (*ibid.* [i.] 11, 209).

When freshly collected the juice consists of a wet granular mass of a pinkish colour, from which there collects in the bottom of the vessel a dark coffee-coloured acid liquid 'pasewa' or 'pussewah.' More of this liquid is separated by draining, and the opium is then carefully dried by exposure to the air, but protected from the rays of the sun. The drying is continued some three or four weeks until the moisture is reduced to 30 p.c., the amount allowed by the Bengal regulations. In this state it arrives at the Government factory, where it is examined physically and chemically, and if satisfactory is admitted. In the factory great care is taken, by mixing low and high quality opiums, to send out a uniform product. It is manipulated into balls, and covered with poppy petals, which have been dried carefully. The petals are made to adhere together into a sort of shell by means of a liquid called 'lewa' or 'lewah,' made partly of opium and partly of 'pasewa.' The spherical cakes, which have a diameter of about six inches, and not unlike in appearance a 24 lb. shot, are rolled in poppy 'trash,' powdered stalks, capsules, and leaves, put into earthenware moulds and exposed to the sun. If blisters form, the cake shells are opened, the gas allowed to escape and then tightly closed again. After three days, about the end of July, the cakes are put into frames and exposed to the air. They there remain, with constant watching, until October, when they are packed in chests, which contain wooden compartments for 40 cakes, and the interstices are loosely filled with poppy 'trash.' The chests, which contain 160 lbs., are then ready for exportation (Eatwell). The so-called medicinal (Benares) opium sent to this country in recent years is placed in paper bags and packed in a chest without compartments, each chest containing 80 cakes of 2 lbs. each. The moisture content of this quality is from 12·5 to 15 p.c.

That which is consumed in India, 'abkari' opium, is prepared somewhat differently. It is dried by exposure to the sun until it contains only 10 p.c. of moisture, in which condition it admits of being moulded like wax. It is made into square bricks about 2 lbs. in weight, wrapped in oiled paper and packed in boxes furnished with suitable compartments. Except that the aroma is not quite so good, 'abkari' opium is equal in quality to that prepared for export (Eatwell, Pharm. J. [i.] 11, 269, 306, 359).

The opium of Malwa and other native districts is not so uniform in quality as that of the Government factories. Malwa opium contains only about 5 p.c. of moisture, and it is sent out in bricks or rounded masses which are not incased in poppy petals.

The percentage of morphine in Indian opium is much less than that found in the opium of Asia Minor. That which has reached this country during recent years consisted of 'medicinal' and 'abkari' opium, both from the Benares factory. Assayed by the British Pharmacopœia method, the morphine content was found to be remarkably uniform over a wide range of samples, varying from 7 to 8 p.c. on the undried drug.

Small quantities of morphine salts sometimes reach this country from India. They are made at the Government laboratories at Ghazipur from opium which has been confiscated on account of adulteration, and are not likely to become an important article of commerce (J. Soc. Chem. Ind. 1889, 917).

China.—Until the prohibition, in 1913, the Chinese consumed a good deal of the opium exported from India, Asia Minor, and Persia, in addition to that produced in China; but for some years prior to this date, the trade had been a diminishing quantity in accordance with the policy of the Chinese Government. It is not possible to estimate the amount produced in China, but some idea of the enormous increase may be gathered from consular and other reports. The various attempts of the Chinese Government to prohibit the manufacture of opium have had little effect. It was about 1830 that it began to be produced in notable quantities. In 1869, in a Report on the Trade of Hankow, addressed to the inspector-general of customs at Peking, the annual yield of the three provinces Yunnan, Kweichow, and Szechuen, was estimated at 41,000 peculs. In the same year it was reported that two-thirds of Szechuen and one-third of Yunnan was devoted to the poppy (Calcutta Blue Book, 205). In 1882 the annual production in the south-west of China, chiefly the provinces of Szechuen and Yunnan, was estimated at over 200,000 peculs, or more than twice the whole importation from India (Pharm. J. [iii.] 13, 225; *cf.* J. Soc. Chem. Ind. 1890, 74). In 1885 the imports of Indian opium in Manchuria had fallen to only 5 p.c. of what they were in 1866, its place being taken entirely by the native drug (Pharm. J. [iii.] 18, 280). In 1887 the district of Wenchow was occupied almost entirely in the production of opium. The country, viewed from a hill-top, was, in many places, one vast brilliant mass of poppy, with here and there a patch of green (J. Soc. Chem. Ind. 1888, 409). The consul at Niew Chang, in Manchuria, reports in 1889 that, although twenty years before 2635 peculs of Indian opium supplied the whole province, at that time the port of Yingtzu alone consumed 3744 peculs annually. This enormous demand was being met almost entirely by the native drug.

Opium is cultivated chiefly in Szechuen, Yunnan, and Kweichow, to a less extent in Shanse, Shense, and Shantung, also in eastern Mongolia, and in Manchuria. The development of the poppy cultivation has been so great in many parts of China that it has seriously interfered with the supply of cereals. For this reason, since the famine, it has been prohibited in Shense, Honan, and Chihli. In Kwangtung the soil and climate are not suitable, and in Fuhkeen the production of sugar is equally or more remunerative (Holmes). In Szechuen, the poppy is a winter crop, and may be gathered in time to allow rice to be planted, and thus not interfere with the summer produce. The yield of opium is about 12 lbs. to the acre. Every part of the plant has a use, if only for manure, and thus the total return amounts to about double that of cereals. As soon as the summer crop is reaped, the soil is prepared and manured with night-soil. The seeds are sown in December, in drills 1½ foot apart, the white poppy being the most commonly cultivated in the low grounds. After a month, when the plants are a few inches high, the rows are thinned and banked up with earth. In March or April the flowering takes place, and at this time the roots are again well manured with night-soil. The capsules are slit in April or May (Pharm. J. [iii.] 13, 225). According to Thorel, the scarification and collection is precisely the same as that carried on in India. Some Szechuen specimens seem to have been collected with the use of oil as in Malwa (Flück. a. Hanb.).

Yunnan and Szechuen opium is made into flat cakes and wrapped in white paper. It is darker and softer than that of Persia, which it resembles. Chekeang is a treacly extract sold in 2 to 4 lb. jars. The product of Shense was supposed to resemble in flavour the highly-prized Patna opium. Yunnan ranks next and then Szechuen (Holmes). A specimen of Chinese opium, examined by Jamieson, contained:—Moisture, 18 p.c.; morphine, 5·3 p.c. (or.

7·2 p.c. in the dried drug); narcotine, 7·5 p.c.; ash, 7·5 p.c. (Report on Trade of Hankow). Authentic specimens examined by Sheppard gave the following percentages of morphine in the dried opium: Szechuen, 2·2; Kweichow, 2·5; Yunnan, 4·1; Kansu, 5·1. Eatwell in Szechuen found 3·3 and in Kweichow 6·1. Sheppard found 5 to 14 p.c. of moisture and 36 to 53 p.c. of extract soluble in water (Fluck. and Hanb.).

Mozambique and Algeria.—In 1877 a Portuguese company was founded to commence the opium culture in Mozambique (Pharm. J. [iii.] 8, 1007; 10, 68, 13, 448). In 1882, according to Guyot, some three hundred labourers were employed in cultivating Zambesi opium between the Muto and Quaqua rivers. The yield compares favourably with that in India. The product is said to be largely admixed with foreign substances before being made into 500 gram balls, which are packed in boxes containing poppy 'trash,' and covered with indigenous cotton (Compt. rend. 95, 798). These balls are sometimes seen in the English market. According to more recent advices, the company has been obliged to go into liquidation, and the cultivation has been abandoned (Pharm. J. [iii.] 21, 87). Opium has been collected in Algeria in small quantity since 1828 (*ibid.* [i.] 15, 348). A dried specimen examined by Guibourt contained 12·1 p.c. of morphine (Jahrb. 1862, 374; Aubergier found 1·5 to 17·8 p.c. (Ann. Chim. [iii.] 20, 303).

Australia.—The production of opium commenced about 1868, and the first specimen reached this country from Victoria, and was examined by Morson in 1869. It contained, according to Hood, 2 p.c. of morphine and 8 p.c. of narcotine (Pharm. J. [iii.] 1, 272). Specimens containing 4·2 to 7·1 p.c. of morphine were sent to England in 1870. They were produced in the village of Sunbury, near Melbourne (Hood). About this time the cultivation was commenced in Gippsland, and opium containing 9 p.c. of morphine, 4 p.c. of narcotine, and 6 p.c. of meconic acid, was obtained (Ward, *ibid.* [iii.] 1, 543). The Toowoomba district in Queensland also furnished some good specimens (*ibid.* [iii.] 1, 972).

The chief part of colonial opium in the Melbourne market comes from the Bacchus Marsh district, where the cultivation has been carried on for years. The sowing takes place at three periods, about the first week in May, the second or third week in June, and the latter part of July. By this means parts of the crop mature in succession. The average yield is 15 to 25 lbs. to the acre, but in a good season as much as 30 to 40 lbs. are obtained. In Europe the average yield to the acre is 25 lbs., and in India 30 to 40 lbs. When the capsules are ready, two incisions are made horizontally, halfway round, and the juice which exudes is collected the next morning. A few days later other incisions are made, until the capsule is exhausted. The opium is manipulated into balls and carefully dried. In quality it approximates to the product of Asia Minor. A specimen gave 11·5 of morphine from the dry drug. Another from Queensland contained 9·8 p.c. (Matthews, Austral. J. Pharm. Nov. 1887).

Europe and North America.—Attempts have been made in most European countries, in Greece, Italy, Spain, France, Switzerland, Germany, England, and Sweden, to cultivate opium, and the results have shown that, providing the soil selected is suitable, and the rainfall not excessive, it is possible, in all these countries, to produce opium equal to that of Asia Minor. The most important European experiments have been conducted in France. A product called 'affium' has been made at Clermont-Ferrand, which is said to contain uniformly 10 p.c. of morphine; but it has not become an important article of trade (Flück. a. Hanb.; Aubergier, Pharm. J. [iii.] 15, 693). Some interesting investigations have been made in the neighbourhood of Amiens, where specimens of dry opium were produced containing 16 and 20 and still higher percentages of morphine. It was observed by Descharme that the morphine diminished when the juice was slowly dried, and the peculiar odour of the drug is ascribed to a species of fermentation (J. Pharm. Chim. [iv.] 6, 222). Guibourt found the percentage of morphine in French opium to vary from 12·1 to 22·8, the latter being the highest proportion of morphine ever recorded (*ibid.* [iii.] 41, 184, 201). Other analyses of French opium give 17·6 p.c. (Descharme, Compt. rend. 40, 34); 17·5 (Chevallier, Fluck. a. Hanb.); 8·2 (Roux, J. 1855, 717); 11·1 to 11·9 (Petermann, Jahrb. 1866, 704). German opium from Erfurt contained 16·6 and 20 p.c. (Biltz, Gm. 16, 415); from Wurtemberg, 12 to 15 p.c. (Hesse, Fluck. a. Hanb.); and from Silesia, 9 to 10 p.c. (Hesse).

Experiments have been carried out on the cultivation of poppies for opium production in the gardens of the Pharmaceutical Institute of the University of Berlin. The amount of opium obtainable from poppies in that latitude is satisfactory; but the cost of collecting it proves to be too high (Thoms, Zeitsch. angew. Chem. 21, 2208). The poppy is rarely grown in Russia, although there are many districts with a suitable soil and climate. Samples of Russian opium from the Ssemiretschinsky district contained about 7·5 p.c. of morphine (Goldberg, Chem. Zeit. 25, Rep. 367).

Experiments in North America led to the same results as in Europe. Specimens from Vermont contained 15·75 p.c. of morphine (Procter, Amer. J. Pharm. [iii.] 18, 124); from Illinois, 8·75 p.c. (Kennedy, *ibid.* [iv.] 1, 6); and from California, 7·75 p.c. (Maisch, *ibid.* [iv.] 3, 103).

For the figures given on p. 712 relating to the trade in opium, acknowledgment is made to the Director of the Imperial Institute.

EXPORTS OF OPIUM FROM PERSIA IN 1913.

(from British Consular Reports.)

		lb.
Through	Mohammerah	163,520
,,	Bushire	309,126
,,	Bunder Abbas	none recorded
,,	Khorassan	159,016
		631,662

Microscopic examination of opium and the constituents extracted by solvents (Deane and Brady, Pharm. J. [ii.] 6, 234; 7, 183). Examples of analyses: Persian opium (W. D. Howard, *ibid.* [iii.] 6, 721); Australian opium (Ward,

IMPORTS OF OPIUM INTO THE UNITED KINGDOM.

(From the 'Annual Statement of the Trade of the United Kingdom.')

	Quantities.		Values.	
	1915.	1916.	1915.	1916.
From—	lb.	lb.	£	£
India	149,004	455,376	151,730	354,376
Hong Kong	13,720	8,058	14,019	8,983
Persia	493,894	193,283	496,854	228,051
European Turkey	192,618	27,651	240,510	45,090
Asiatic Turkey	21,671	1,760	21,783	3,000
France	—	822	—	1,326
Other countries	80,806	7,930	95,776	12,408
	951,713	694,880	1,020,672	653,234

EXPORTS OF OPIUM FROM INDIA.

(From the 'Accounts of the Sea-borne Trade of British India.')

	Quantities.		Values.	
	1915–16[1]	1916–17[1]	1915–16[1]	1916–17[1]
To—	Chests	Chests	Rupees[2]	Rupees[2]
United Kingdom	199	—	361,500	—
Straits Settlements	605	239	1,017,250	591,025
Java	1,835	1,965	3,120,800	5,129,650
Siam	1,700	1,200	2,837,450	2,876,700
Indo-China	2,035	3,440	3,350,650	8,190,395
Hong Kong	734	450	1,187,330	724,175
Japan	1,080	963	1,808,250	2,383,070
Mexico	460	—	779,575	—
Other countries	138	453	239,035	1,070,165
Total chests	8,786	8,710	14,701,840	20,965,180
= cwt.	12,878	=12,760	= £980,123	=£1,397,679

ibid. [iii.] 1, 543; Matthews, Austral. J. Pharm. Nov. 1887); Vermont opium (Procter, Amer. J. Pharm. [iii.] 18, 124; Flückiger, Jahr. 1869, 797; Pharm. J. [ii.] 10, 208); Indian and Chinese opium (Browne, *ibid.* 84, 452; van Itallie and Korbosch, Arch. Pharm. 248, 609).

Physiological action and uses.—Opium is without doubt the most important remedy available for use in medicine. Its action on man is chiefly on the brain, producing sleep. In doses of a grain or less, a stage of slight excitement supervenes during which the individual can control his energies. In 1 to 2 grain doses the stage of excitement is short and is succeeded by deep sleep, after which there is nausea and headache. If large doses of 3 grains or more be administered the excitement is very short and is followed by sleep which becomes more and more comatose until the patient cannot be aroused. If death takes place the respiration ceases first. Opium is used for the alleviation of pain, either generally or locally, for the production of sleep, or for reducing the irritation of various organs. Its special applications in the treatment of disease are almost endless (*cf.* Brunton, Pharm. Therapeut. 1887, 852).

The action of opium in stimulating and then depressing gives rise to the desire to repeat the dose. In this way the habit of 'opium eating' is contracted. The worst effects of opium are thus obtained. It deranges the nervous system, and impairs the intellectual and moral and finally also the physical powers. De Quincey's description of his own experience is well known.

But by far the largest quantity of opium is used for smoking. The habit is believed to have originated in Persia, but it is in China, where it prevails to the greatest extent at the present day, where, indeed, its use appears to be almost as widely diffused as the use of tobacco in Europe. For smoking the opium undergoes a process of preparation which is a business in itself. In Hong Kong, according to McCallum, the opium is extracted by boiling with water and the clear solution is evaporated until it attains the consistence of treacle (Pharm. J. [iii.] 11, 229; 12, 446). The Chinese in California first put the opium through a series of roasting processes which are said to destroy its stickiness and render it more easily extracted by boiling with water (Calvert, *ibid.* [iii.] 120, 148). The Chinese recognise four varieties of opium:—(1) Raw opium; (2) Prepared opium, the treacly extract described; (3) Opium 'dross,' the scrapings of the opium pipe, which are said to be strong, hot, of inferior flavour; (4) Opium 'dirt,' the exhausted marc after extraction with water (McCallum).

'The whole operation of opium-smoking is described in a letter which accompanied an opium-smoker's set of apparatus in 1882 from Canton to Kew. The pipe has a flat bowl made of metal with a very small opening. A drop of the soft opium is taken on the point of a 'dipper' and dexterously roasted in the flame of a little lamp until with constant burning it has the appearance of burnt worsted. Then, first warming the bowl of the pipe, the drug, about the size of a hemp-seed, is placed about the opening in the bowl, the pipe taken in the mouth and the opium ignited. The smoke is partly swallowed or inhaled and partly exhaled by the mouth and nose. The preparation for smoking occupies 5 or 10 minutes, but the actual smoking only about 30 seconds (Sampson, *ibid.* [iii.] 11, 22).

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[1] Year ended 31st March.

[2] 15 rupees = £1.

The physiological action of opium smoked in this way is clearly quite different from what it is when taken in the stomach. It is noteworthy that those opiums most highly prized for smoking contain a small percentage of morphine. It would seem that, notwithstanding the serious view of the effects of opium-smoking taken by the Chinese Government and held by many Europeans, the habit is not more injurious than the use of other stimulants. Opium in the East seems to perform the same function that alcohol does in the West, and, as far as can be ascertained, with about the same good and bad effects (*cf.* Birdwood, Pharm. J. [iii.] 12, 500; Spence, *ibid.* [iii.] 13, 226; McCallum, *ibid.* [iii.] 14, 27; James, *ibid.* [iii.] 18, 280).

Opium occupies an unique position in respect of the number of alkaloids which it contains; these are dealt with in detail below:—

Morphine Group (*Morphine, Codeine, Thebaine*).

Morphine $C_{17}H_{19}O_3N{\cdot}H_2O$, the first known vegetable alkaloid was isolated from opium about the year 1807 by Sertürner. It is contained in minute amounts in several other plants belonging to the natural order *Papaveraceæ*.

Preparation.—Morphine exists in opium in the form of two soluble salts (meconate and sulphate), so that extraction with water removes the whole of the alkaloid.

Gregory's method for the manufacture of morphine from opium consists in extracting the drug with lukewarm water, mixing the liquid with excess of chalk, and evaporating to a small volume. Slight excess of calcium chloride is now added, the liquid diluted with water, and the precipitated resin, calcium meconate, &c., filtered off. On concentrating the liquid the hydrochlorides of morphine and codeine crystallise out. These are dissolved in water, the solution decolorised with charcoal and decomposed with excess of ammonia, which precipitates morphine containing a little codeine. For complete separation the codeine may be extracted by one of the solvents, in which it is much more soluble than morphine, *e.g.* ether or benzene.

Properties.—Small rhombic prisms or silky needles containing $1H_2O$, which is gradually lost at 100°, more rapidly at 120°. At higher temperatures (about 230°) morphine melts with some decomposition, and afterwards a part of the alkaloid sublimes, together with some of its decomposition products. Slightly soluble in water, 1 in 10,000 at 10°; 1 in 5000 at 20° (Chastaing, Bull. Soc. chim. 1882, [ii.] 37, 477); more soluble in boiling water (1 in 500). Soluble in absolute alcohol (1 in 100 at 10°; 8·6 in 100 at b.p.), less so in aqueous alcohol (1 in 100 at 15°; 1 in 36 at b.p.). Less soluble in amyl alcohol (1 in 400 at 11°; 1·1 in 50 at 78°). Very slightly soluble, or nearly insoluble in ether, benzene, chloroform, or light petroleum (Florio, Gazz. chim. ital. 1883, 13, 496; *cf.* Müller, Apoth. Zeit. 1903, 18, 257, and U.S. Pharmacopœia, 8th ed.). Readily soluble in solutions of fixed alkalis, especially when warm; less soluble in aqueous ammonia (rel. dens. 0·97) (1 in 177 at 15°). Lævo-rotatory, in methyl alcohol $[\alpha]_D^{23}=130{\cdot}9°$, in aqueous soda $[\alpha]_D=-70{\cdot}23°$; more strongly lævo-rotatory in neutral or acid solution (Hesse, Annalen, 1875, 176, 190).

Morphine is a strong monacidic base; its alcoholic solution is alkaline to litmus. Dilute acids readily dissolve morphine, and the salts are generally easy to crystallise. The hydrochloride $B{\cdot}HCl,3H_2O$ is a well-crystallised salt, soluble in water (1 in 24 at 15°), less soluble in alcohol (Hesse, *l.c.*). This salt and the sulphate, acetate, and tartrate, &c., are used in medicine. The platinichloride $(B{\cdot}HCl)_2PtCl_4$ is crystalline. The alkaloid and its salts have a bitter taste, and when administered in small doses exert a powerful narcotic action; in larger doses they are posionous.

Reactions and constitution.—Solution of ferric chloride, almost free from acid, produces with the alkaloid, and with neutral solutions of its salts, a deep-blue coloration, which is discharged by strong acids. This reaction is characteristic and delicate in neutral or nearly neutral solutions. Strong sulphuric acid, free from nitric acid, does not colour morphine unless the mixture is warmed, when a brown coloration is produced. Nitric acid dissolves the alkaloid, with the production of a deep-red colour. If the morphine is first dissolved in strong sulphuric acid and then a drop of nitric acid added, a carmine coloration is observed. Morphine is a powerful reducing agent, converting ferric salts into ferrous salts, solution of potassium ferricyanide into potassium ferrocyanide, and precipitating the metals from solutions of silver nitrate, and gold and platinum chlorides. Since it reduces aqueous iodic acid, liberating iodine, this reaction is often utilised as a test for morphine, the iodine being detected in the usual manner. The salts of morphine also liberate iodine from aqueous iodic acid. Morphine is liable to be mistaken for emetine if colour reactions alone are relied on for its identification (*see* under *Emetine*, Vol. III. p. 658; and Allen and Scott-Smith, Analyst, 1902, 27, 345)

Morphine is a tertiary base which combines with 1 mol. prop. of alkyl iodide.

A dibenzoyl and a diacetyl derivative (*heroine*) of morphine have been prepared, whence it may be inferred that the alkaloid contains two hydroxyl groups (Wright, Chem. Soc. Trans. 1874, 27, 1031; Wright and Beckett, *ibid.* 1875, 28, 15; Wright and Rennie, *ibid.* 1880, 37, 610). One of these hydroxyl groups is probably attached to a benzene nucleus, since it has phenolic properties; thus morphine dissolves in alkalis, forming metallic derivatives, in which one atom of hydrogen of the morphine is replaced by metals (Chastaing, Compt. rend. 1882, 94, 44).

When morphine is heated with hydrochloric acid (25 p.c.) in a closed tube at 140°–150°, a molecule of water is separated and *apomorphine* $C_{17}H_{17}O_2N$ is produced. It is isolated by adding sodium bicarbonate in excess to the acid liquid, and shaking with ether, which dissolves the 'apomorphine.' The free base is usually amorphous; it is slightly soluble in cold water, and unstable when exposed to air, absorbing oxygen, especially in presence of alkali, with the production of a green, and afterwards a red, colour. The hydrochloride B·HCl is crystalline and is used in medicine. The properties of apomorphine appear to show that the base still contains the phenolic hydroxyl present in morphine in addition to a second due to the fissure of the ring containing the 'indifferent' oxygen. Its physiological action differs entirely from that of morphine, since it produces no narcotic effect, but acts as a powerful emetic (Matthiesson and Wright, Proc. Roy. Soc. 1868–1869, 17, 455; Marmé, Zeitsch. anal. Chem. 1885, 24, 643; Pschorr, Jaeckel and Fecht, Ber. 35, 4377).

Alkaline solutions of morphine absorb oxygen from the air, which converts the morphine into *pseudomorphine* (oxydimorphine) $C_{34}H_{36}O_6N_2$, a base which also results from the action of weak oxidising agents on morphine, and is found in small quantity in opium (Hesse, Annalen, 1867, 141, 87; 1875, 175, 195; 1884, 222, 234; 1886, 234, 255). It is not poisonous.

The reactions, which are of primary importance as regards the constitution of morphine, and the closely related alkaloids, codeine and thebaine, are as follows:—

1. Of the three oxygen atoms in morphine one is phenolic, and on methylation gives rise to codeine; the second is alcoholic; the third oxygen atom is non-reactive, and is present in a heterocyclic nucleus.

2. The nitrogen atom is tertiary.

3. On distillation with zinc-dust morphine yields phenanthrene.

4. With methyl iodide morphine furnishes codeine methiodide; this on warming with silver hydroxide gives codeine methylhydroxide $MeO(HO)\cdot C_{16}H_{14}O\cdot NMe_2OH$, which immediately decomposes, giving methylmorphimethine

$$MeO(OH)\cdot C_{16}H_{13}O\cdot NMe_2$$

by loss of H_2O. This base when heated with hydrochloric acid or acetic anhydride is decomposed in part, forming methylmorphol and hydroxyethyldimethylamine—

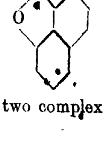
$$\left.\begin{matrix}HO\\OMe\end{matrix}\right>C_{16}H_{13}O\cdot NMe_2=\left.\begin{matrix}HO\\OMe\end{matrix}\right>C_{14}H_8+C_4H_{11}ON$$

Methylmorphimethine. Methylmorphol Hydroxyethyldimethylamine.

Methylmorphol is known to be 4-hydroxy-3-methoxyphenanthrene (Pschorr and Sumuleanu, Ber. 1900, 33, 1810). Hydroxyethyldimethylamine probably results from the addition of water to vinyldimethylamine first liberated thus

$$NMe_2\cdot CH:CH_2 \rightarrow NMe_2\cdot CH_2\cdot CH_2OH$$

It follows from the above that morphine must be built up from the complexes



and $—CH_2\cdot CH_2\cdot NMe—$

The two complexes have been 'assembled' in various ways, but Pschorr's formula is that now generally accepted (*see* p. 716 under *Thebaine*).

Various derivatives of morphine have assumed considerable importance in recent years. Diacetyl-morphine (m.p. 169°–172°C.) and its hydrochloride (m.p. about 230°C.) known originally as heroine and heroine hydrochloride respectively; the latter is now 'official' in the British Pharmacopœia under the designation 'diamorphine hydrochloride.' Ethylmorphine hydrochloride (m.p. 122°–123°C.) or 'dionine' and benzylmorphine hydrochloride or 'peronine' are the hydrochlorides respectively of the ethyl and benzyl ethers of morphine.

Detection.—Morphine affords precipitates with most of the alkaloidal reagents. It may be identified by means of the properties and reactions described above. The characteristic reactions of morphine can, however, only be relied on when a nearly pure alkaloid has been experimented with. Unfortunately, morphine is one of the most difficult alkaloids to separate from much organic impurity, especially when it is present only in minute quantity, as is generally the case in toxicology. Since the internal administration of opium, and not of morphine itself, is often the cause of poisoning, the existence of this alkaloid may be confirmed by detecting meconic acid, which is easy to recognise.

For a detailed account of the qualitative reactions of morphine, *see* Marmé, *l.c.*

Estimation.—The following method for the estimation of morphine in opium is official in the British Pharmacopœia, 1914: 8 grms. of opium in No. 50 powder, dried at 60°, are mixed with 2 grms. of slaked lime, and stirred in a mortar with 20 c.c. of water. The mixture is diluted with 60 c.c. of water and occasionally stirred during half an hour. To 51 c.c. of the filtered liquid (representing 5 grms. of opium) 5 c.c. of 90 p.c. alcohol and 25 c.c. of ether are added, the whole shaken, 2 grms. of ammonium chloride then introduced and the mixture again well shaken during half an hour. After the lapse of 12 hours the morphine will have crystallised out. Decant the ethereal layer and filter it through a small counterbalanced paper. Add 10 c.c. of ether, agitate gently, again decant and filter the ethereal layer and then wash the filter paper with 5 c.c. of ether and dry. Now filter off the watery liquid, keeping the morphine in suspension and finally wash with a saturated solution of morphine in water. The crystals of morphine are dried first at 60° and then at 115° for two hours and weighed. 0·2 grm. of the crystals is then dissolved in 10 c.c. of N/10 sulphuric acid and titrated back with N/10 sodium hydroxide, using methyl orange as indicator. The weight of anhydrous morphine as indicated by titration +0·051 grm. (correction for loss) should be 0·475 to 0·525 grm., *i.e.* 9·5 to 10·5 p.c.

For an account of other methods which have been proposed, v. Allen's Organic Analysis, 4th ed. vol. vi.

For the estimation of morphine in tincture of opium (laudanum) the following method may be employed: 40 c.c. of the laudanum are evaporated to 10 c.c. on the water-bath, and the residue thoroughly mixed with 1 grm. of calcium hydroxide, and diluted to 41 c.c.

with water. The liquid is then filtered, and 25 c.c. of the filtrate (representing the same quantity of laudanum) are mixed with 2·5 c.c. of alcohol (90 p.c.), 15 c.c. of ether, and 1 grm. of ammonium chloride. The mixture is well shaken and allowed to remain for 12 hours. The crystals of morphine, which will have separated, are collected, with the precautions described above for the estimation of morphine in opium, 8 c.c. of ether being used to rinse the contents of the bottle and 5 c.c. to wash the filter paper. After drying finally at 115° and weighing, 0·2 grm. of the crystals is titrated as above. The weight of anhydrous morphine indicated by titration +0·025 grm. (correction for loss) should be 0·2375 to 0·2625 grm., *i.e.* 0·95 to 1·05 grm. in 100 c.c.

Codeine $C_{18}H_{21}O_3N{\cdot}H_2O$ exists in Turkey opium in the proportion of about 0·75 p.c., while in the Persian and Indian varieties the average is about 2·25 p.c.

Preparation.—The mixed hydrochlorides of morphine and codeine, having been separated from opium by Gregory's method (*see Preparation of Morphine*), and the morphine precipitated by ammonia, the alkaline filtrate, which contains codeine hydrochloride, is evaporated to a small volume and precipitated by potash. The codeine is purified by crystallisation from ether or from water. Codeine, being the methyl ether of morphine, may be prepared from the latter by heating it with alcoholic soda and methyl iodide (Grimaux, Ann. Chim. 1882, [v.] 27, 273; Hesse, Annalen, 1884, 222, 210), or by the action of potassium methyl sulphate on morphine dissolved in methyl alcohol.

Properties.—Large rhombic crystals from water with $1H_2O$, which melt in boiling water; small anhydrous crystals from ether, m.p. 155°. Lævo-rotatory $[\alpha]_D - 137{\cdot}75°$ in alcohol. Slightly soluble in cold water, more soluble in hot water, alcohol, ether, or benzene; sparingly soluble in light petroleum. The aqueous solution is strongly alkaline. Codeine is a monacidic base; the principal salts are crystalline and soluble in water. In physiological action codeine and its salts resemble morphine, but are less poisonous.

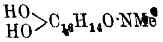
Reactions and constitution.—Codeine is distinguished from morphine by not giving the colour reaction with ferric chloride, and by producing with nitric acid a yellow, and not a red, colour. Concentrated sulphuric acid does not colour codeine except after prolonged standing, but if a trace of nitric acid or ferric salt is added to the mixture it becomes blue. For an account of the qualitative reactions of codeine, *see* Marmé, Zeitsch. anal. Chem. 1885, 24, 648. The decomposition products of codeine are, for the most part, analogous to those of morphine (p. 714).

Estimation.—The following process has been devised by Andrews (Analyst, 1911, 36, 489). Dry opium (12 grms.) is exhausted by successive portions of cold water, the filtrate made up to 100 c.c., and 20 c.c. of 20 p.c. lead acetate solution added, to remove colouring matter and some narcotine. The mixture is kept over-night, then passed through a filter paper in a Buchner funnel, and from 100 c.c. of the filtrate (10 grms. of opium) the excess of lead is removed by hydrogen sulphide, and this in turn removed by a current of air. The washings from the lead sulphide precipitate are collected separately, evaporated to a small bulk, and added to the main filtrate, which should then not exceed 130 c.c. To this 20 c.c. of a 20 p.c. solution of sodium salicylate are added, and the flask containing the mixture corked and shaken. A resinous precipitate separates leaving a nearly clear liquor, which is passed through a small pleated filter, into a beaker containing a few crystals of thebaine salicylate, to facilitate the separation of this salt from the filtrate, which is well stirred to assist this operation. After standing over-night the liquid is again passed through the same pleated filter and the treatment repeated until no further deposition of solid matter takes place. The final filtrate and washings, concentrated to about 10–15 c.c. on a water-bath, are transferred while still warm to a glass separator (No. 1), the washings of the dish being placed in a second separator (No. 2). The contents of No. 1 are washed with three successive portions of ether, each portion being in turn also used to wash the contents of No. 2. The latter are finally added to separator No. 1, and 10 c.c. of a 20 p.c. solution of caustic soda added, to keep the morphine dissolved. This strongly alkaline liquid is extracted four times in succession with rather more than its own volume of ether, each portion of ether, as separated, being washed with 20–30 c.c. of water and finally run into a dry flask containing anhydrous sodium sulphate to dry it. The dry ethereal solution of codeine is distilled in a flask down to a few c.c., which are allowed to evaporate spontaneously, when, as a rule, the codeine separates in well-defined crystals, and after drying can be weighed, the weight being checked by dissolving in excess of N/10 acid and titrating back with N/10 sodium hydroxide, using litmus or methyl-orange as indicator.

Thebaine $C_{19}H_{21}O_3N$ occurs in small quantity (up to 1 p.c.) in opium, and remains in the mother liquor after the separation of morphine and codeine hydrochlorides (p. 713). It is precipitated from this along with narcotine and papaverine by addition of ammonia. The precipitate is dried and dissolved in boiling alcohol. On cooling narcotine and papaverine crystallise out. The filtrate is evaporated to dryness, the residue dissolved in acetic acid, and the solution decolorised with lead acetate. From the filtrate, after removal of excess of lead by hydrogen sulphide, thebaine is precipitated by adding ammonia.

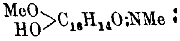
Properties and reactions.—Leafy or prismatic crystals, m.p. 193°. Lævo-rotatory. Nearly insoluble in cold water, slightly soluble in ether, very soluble in alcohol, chloroform, or benzene. Slightly soluble in aqueous alkalis. Thebaine is a monacidic base; the principal salts are crystalline and soluble in water. The alkaloid and its salts are poisonous and exercise a tetanising action, but are less powerful then strychnine and its salts. Thebaine is coloured bright red by concentrated sulphuric acid. It is converted into thebenine when warmed with dilute acids, and is attacked by concentrated hydrochloric acid, with the formation of morphothebaine, isomeric with thebenine $C_{18}H_{20}O_3N$.

CONSTITUTION.—Thebaine is related somewhat closely to morphine and its methyl ether, codeine, as inspection of slightly extended formulæ for the three alkaloids shows—



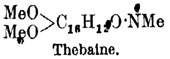
$$\left.\begin{matrix}HO\\HO\end{matrix}\right\rangle C_{16}H_{14}O{\cdot}NMe$$

Morphine.



$$\left.\begin{matrix}MeO\\HO\end{matrix}\right\rangle C_{16}H_{14}O{\cdot}NMe$$

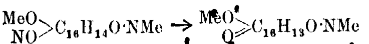
Codeine.



$$\left.\begin{matrix}MeO\\MeO\end{matrix}\right\rangle C_{16}H_{12}O{\cdot}NMe$$

Thebaine.

When codeine is oxidised by chromic acid the alcoholic hydroxyl group is converted into a carbonyl group with the formation of codeinone, thus—



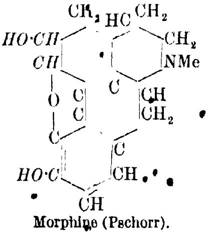
$$\left.\begin{matrix}MeO\\NO\end{matrix}\right\rangle C_{16}H_{14}O{\cdot}NMe \rightarrow \left.\begin{matrix}MeO\\O\end{matrix}\right\rangle C_{16}H_{13}O{\cdot}NMe$$

Codeine. Codeinone.

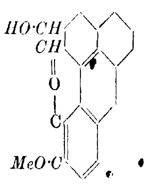
On treatment with dilute acids both thebaine (Howard and Roser, Ber. 1886, 19, 1596; and Freund, *ibid.* 1899, 32, 168) and codeinone (Knorr, *ibid.* 1903, 36, 3074) yield thebenine, whilst with strong acids they furnish the isomeric morphothebaine (*l.c.*). Further, hot acetic anhydride decomposes thebaine (Freund, *ibid.* 1897, 30, 1357) and codeinone (Knorr, *l.c.*) in the following ways (*cf.* Pschorr, Seydel and Stohrer, *ibid.* 1902, 35, 4400)—

$$\left.\begin{matrix}\textit{Codeinone} \rightarrow \text{6-Methoxy : 4 di-hydroxyphenanthrene}\\ \textit{Thebaine} \rightarrow \text{3 : 6-Dimethoxy-4-hydroxyphenanthrene}\end{matrix}\right\} + \text{hydroxyethyl-methylamine}$$

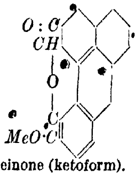
Thebaine must therefore be the methyl ether of an enolic form of codeinone. Accepting Pschorr's formulation of morphine, the three alkaloids, codeine, codeinone, and thebaine, will be represented by the following formulæ in which the variable groups only are shown in the last three (Ber. 1902, 35, 4382; 1905, 38, 3160; 1907, 40, 1984; *cf.* Knorr and others, *ibid.* 1907, 40, 3341, 4891, Wieland and Kappelmeier, Ann. 1911, 382, 306; Freund. Ber. 1905, 38, 3238; 1910, 43, 2128).



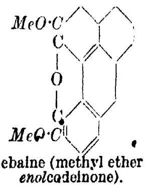
Morphine (Pschorr).



Codeine.



Codeinone (ketoform).



Thebaine (methyl ether of *enol*codeinone).

The precise configuration of the morphine molecule must still, however, be regarded as an open question, and for further information reference may be made to a critical survey by F Faltis (Arch. Pharm. 1917, 255, 85), and Watt (Science Progress, 1909, 279). Compare also Freund, Melber and Schlesinger (J. pr. Chem. 1920, ii. 101, 1); Mannich and Löwenheim (Arch. Pharm. 1920, 258, 295); Freund and Speyer (Ber. 1920, 53, 225); Skita (*ibid.* 1921, 54, 1560); Speyer and Siebert (*ibid.* 1519); Speyer and others (D. R. P. 338147); Abst. Chem. Soc., 1921, i. 124, 125, 684, 685, 803).

Thebaine treated in aqueous alcoholic solution with excess of molecular hydrogen, using colloidal metallic catalysts of the platinum group, yields a base $C_{18}H_{23}O_3N$, crystallising in leaflets (from alcohol), m.p. 145°–150°; precipitated from solutions of its salts by sodium carbonate or ammonia. Contains one methoxyl group and has the character of a ketone (D. R. P. 338147). When oxidised by hydrogen peroxide, thebaine yields methyl alcohol and a tertiary base possessing ketonic properties: this base is probably allied to codeinone which contains one oxygen atom less, whence it is termed oxycodeinone (Freund and Speyer, Munch. med. Woch. 1917, 64, 380).

Narcotine Group (*Narcotine*, *Gnoscopine*, *Hydrocotarnine*, *Narceine*).

Narcotine $C_{22}H_{23}O_7N$ usually occurs to the extent of about 5–6 p.c. in Asia Minor opium, but in larger quantity in Indian and Persian opiums. Unlike most alkaloids, narcotine appears, as a rule, to exist in the plant in the free state, and not as a salt.

Preparation.—If the opium is extracted with water in order to isolate the morphine, &c., the greater part of the narcotine remains undissolved, since this alkaloid is nearly insoluble in water. By exhausting the residue with dilute hydrochloric acid, the narcotine is removed as hydrochloride, and from the solution of this salt the base may be precipitated by sodium bicarbonate, and crystallised from alcohol. Or the narcotine may be extracted from the opium by boiling it with ether; *see* also Hesse, Annalen, Suppl. 8, 284.

Estimation.—Narcotine is most readily estimated in opium by drying the drug at 100° and then extracting a weighed quantity with hot ether. From the ether solution the alkaloid may be extracted by repeated agitation with dilute sulphuric acid, and may be obtained clean by adding alkali and re-extracting with ether.

Properties.—Prismatic crystals, m.p. 174°–175°. Almost insoluble in water (1 in 25,000 at 15°, 1·1 in 7000 at 100°); soluble in alcohol (1 in 100 at 15°, 1 in 20 at b.p.); ether (1 in 166 at 16°), and in benzene (1 in 22 at 15°); very soluble in chloroform (1 in 2·69 at 15°); slightly soluble in amyl alcohol or light petroleum, dissolves in lime or baryta water, and slightly in aqueous ammonia. Lævo-rotatory, $[\alpha]_D = -185°$ in alcohol (Hesse, Annalen, 1875, 176, 192), $-199{\cdot}9°$ in chloroform (Perkin and Robinson, Chem. Soc. Proc. 1910, 26, 131). The solution in dilute acids is dextro-rotatory. Narcotine is a feeble monacidic tertiary base; its aqueous solution is neutral to litmus. The principal salts crystallise with difficulty, their aqueous solutions are acid, and are decomposed, with separation of narcotine when evaporated. The free alkaloid may even be extracted from the aqueous solution of some narcotine salts by agitating with ether or chloroform. In larger doses than are necessary in the cases of morphine and codeine, narcotine and its salts exert a narcotic action.

Reactions and constitution.—Concentrated sulphuric acid dissolves narcotine, and the solution soon becomes yellow; on warming a rapid transition of different colours is observed, the mixture becoming orange-red, blue, and finally purple. Nitric acid dissolves the alkaloid with a yellow colour.

When heated with hydriodic acid narcotine furnishes three molecular proportions of methyl iodide and *nornarcotine* $C_{19}H_{17}O_7N$ or

$$C_{19}H_{14}(OH)_3O_4N$$

The less energetic action of hydriodic acid produces one molecular proportion of methyl iodide, and *dimethylnornarcotine*

$$C_{19}H_{14}(OCH_3)_2(OH)O_4N$$

or two molecular proportions of methyl iodide and *methylnornarcotine* $C_{19}H_{14}(OCH_3)(OH)_2O_4N$.

When heated with water in a closed tube at 100°, or by prolonged ebullition with water, the alkaloid is resolved into *opianic acid*

$$C_6H_2(OMe : OMe : COOH : CHO = 1 : 2 : 3 : 4)$$

and *hydrocotarnine*

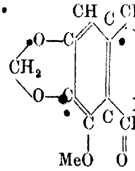
$$(C_{22}H_{23}O_7N + H_2O = C_{10}H_{10}O_5 + C_{12}H_{15}O_3N)$$

from which cotarnine $C_{12}H_{15}O_4N$ results by oxidation (Beckett and Wright, Chem. Soc. Trans. 1875, 28, 583). Cotarnine is largely employed in the form of its chloride (stypticin) as an internal styptic (*cf. Hydrastinine*, Vol. III. p. 532).

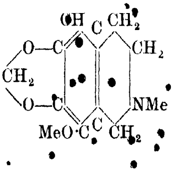
Nascent hydrogen converts narcotine into *meconin* and *hydrocotarnine* $C_{12}H_{15}O_3N$, and on oxidation *cotarnine* and *opianic acid* (*see* above) are formed, the latter by further oxidation becoming *hemipinic acid*

$$C_6H_2(OMe : OMe : COOH : COOH = 1 : 2 : 3 : 4)$$

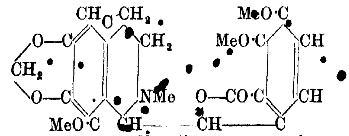
On 'exhaustive methylation' cotarnine yields *cotarnone* $C_{11}H_{10}O_4$, which on oxidation gives *cotarnic acid* $C_{10}H_8O_7$, and this with hydrochloric acid furnishes the methylmethylene ether of gallic acid. From these and other data Roser has assigned the following formulæ to cotarnine, hydrocotarnine, and narcotine (Annalen, 1888, 249, 156, 168; 1889, 254, 334, 351; 1893, 272, 221; *cf.* Freund and Becker, Ber. 1903, 36, 1521):—



Cotarnine.



Hydrocotarnine.



Narcotine.

The synthesis of narcotine has been effected by Perkin and Robinson by treating an alcoholic solution of cotarnine and meconin with potassium carbonate, or by simply boiling an alcoholic solution of these two substances (Chem. Soc. Proc. 1910, 26, 46; Chem. Soc. Trans. 1911, 99, 778; *cf.* Liebermann, Ber. 1896, 29, 184). Cotarnine had been prepared previously by Salway (Chem. Soc. Trans. 1910, 97, 1208) from myristicin. The substance actually produced in Perkin and Robinson's synthesis is the alkaloid *gnoscopine*, isolated from opium by T. and H. Smith (Pharm. J. 1878, [iii.] 9, 82; 1893, [iii.] 52, 794), and which Rabe had suggested (Ber. 1907, 40, 3280; 1910, 43 800; Annalen, 1910, 377, 223) was *dl*-narcotine produced by racemisation of narcotine during its isolation from opium. Natural and synthetic gnoscopines were resolved by crystallising the *d*-camphor-sulphonate into *d*- and *l*-narcotine, the latter identical with the natural alkaloid, by Perkin and Robinson (Chem. Soc. Proc. 1910, 26, 46, 131).

Narceine $C_{23}H_{27}O_8N,H_2O$ occurs in opium to the extent of 0·1 p.c., and is recovered from the mother liquors from which morphine and codeine hydrochlorides have crystallised out, after the removal from these of narcotine, thebaine, and papaverine (p. 713).

Properties.—Crystallises from water or alcohol in prisms or slender needles with $3H_2O$, m.p. 170°, or 140° 145° ($1H_2O$) when dried at 100°. Sparingly soluble in cold water (1 in 1285 at 13°), or cold alcohol (1 in 945 of 80 p.c. alcohol), much more soluble in hot water or hot alcohol. Somewhat soluble in ammonia and alkalis. Optically inactive. Narceine has no marked physiological action. It is a monacidic base and forms well-crystallised salts with acids. It also behaves as a monocarboxylic acid and forms a series of salts with metals (potassium-narceine

$$C_{23}H_{26}O_8NK$$

rosettes of needles), and yields esters with alcohols (narceine ethyl ester hydrochloride

$$C_{23}H_{26}(C_2H_5)O_8N,HCl$$

is crystalline, m.p. 206°–207°). Methyl iodide reacts with narceine to form narceine methyl ester methiodide $C_{23}H_{26}(CH_3)O_8N,CH_3I$, m.p. 193°–194°.

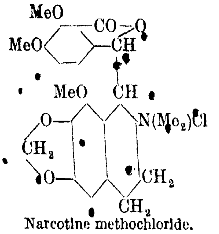
Reactions and constitution.—Narceine gives with chlorine water, followed by ammonia solution, a blood-red coloration. Its constitution is established by the fact that it can be prepared by heating narcotinemethochloride with alkalis. According to Freund this change takes place as shown by the formulæ at top of next page.

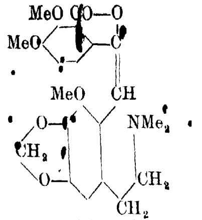
The chief papers relating to narceine are: Pelletier, Annalen, 1832, 5, 163; Anderson, *ibid.* 1853, 86, 182; Hesse, *ibid.* 1875, 176, 198; Roser, *ibid.* 1888, 247, 169; Freund and collaborators, *ibid.* 1893, 277, 6; Ber. 1909, 42, 1084).

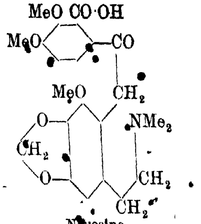
Papaverine Group (Papaverine, Laudanosine, Laudanine, &c.).

Papaverine $C_{20}H_{21}O_4N$. This alkaloid separates with narcotine as described under thebaine (p. 713) and is separated from it by conversion into the acid oxalate, which is sparingly soluble in alcohol, that of narcotine being readily soluble.

Properties.—Prismatic crystals, m.p. 147°.


Narcotine methochloride.


Intermediate product.


Narceine.

Very slightly soluble in hot or cold water; easily soluble in hot alcohol, chloroform, or benzene. Optically inactive. A monacidic base which forms crystalline salts. It is mildly soporific in action.

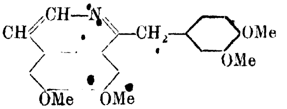
Reactions and constitution.—Sulphuric acid dissolves papaverine in the cold without coloration. Commercial papaverine gives a violet coloration due to the presence of cryptopine (p. 719) (Pictet and Kramers, Ber. 1910, 43, 1329). With sulphuric and iodic acids it gives a purple coloration changing to green.

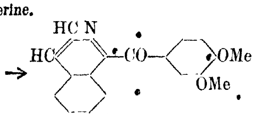
Nascent hydrogen converts papaverine into a dihydride (Pyman, Chem. Soc. Trans. 1909, 95, 1610). When heated with concentrated hydriodic acid it furnishes papaveroline $C_{16}H_{13}O_4N$, together with four molecular proportions of methyl iodide, from which it is inferred that four methoxyl groups are present.

On oxidation with permanganate papaverine yields a large number of products, the principal being *veratric acid*, *metahemipinic* or *dimethoxy-o-phthalic acid* $C_6H_2(OCH_3)_2(CO_2H)_2$, *pyridine-αβγ-tricarboxylic acid*, and *papaveraldine*. According to Dobson and Perkin (Chem. Soc. Trans. 1911, 99, 135) papaveraldine (*see* below) is identical with *xanthaline*, an alkaloid isolated from opium by T. and H. Smith (Pharm. J. 1893, [iii.] 52, 793).

When fused with alkali papaverine affords *veratric acid*, together with *dimethoxy*-iso-*quinoline*.

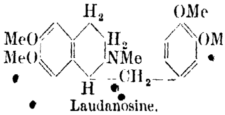
From these and other results Goldschmiedt (Monatsh. 1883, 4, 704; 1885, 6, 372, 667, 956; 1886, 7, 488; 1887, 8, 510; 1888, 9, 42, 327, 349) has concluded that papaverine is tetramethoxybenzyl*iso*quinoline, and this constitution has been established by synthesis of the alkaloid (Pictet and Gams, Compt. rend. 1909, 149, 210).


Papaverine.


Papaveraldine (xanthaline).

Reference should also be made to Pyman and Reynolds (Chem. Soc Trans. 1910, 97, 1320); and Pyman (*ibid.* 1915, 107, 176).

Laudanosine $C_{21}H_{27}O_4N$. When papaverine methochloride is reduced with tin and hydrochloric acid it furnishes *dl-N*-methyltetrahydropapaverine, m.p. 115°, and this on crystallisation of the quinate, separates into the *d*- and *l*-bases, the former being identical with d-*laudanosine* which occurs in opium. It crystallises in needles, m.p. 89°, $[\alpha]_D+103°$ in alcohol and contains four ·OMe groups. Laudanosine is more poisonous than papaverine, and resembles thebaine in physiological action; it exerts no narcotic effect (Pictet and Athanasescu, Ber. 1900, 33, 2346). *dl*-Laudanosine is also formed when *laudanine* $C_{20}H_{25}O_4N$, crystals, m.p. 166°, $[\alpha]_D\pm 0°$, an alkaloid occurring in opium, is methylated, so that it appears to be the methyl ether of laudanine (Hesse, Annalen, 1894, 282, 208; J. pr. Chem. 1902, [ii.] 65, 42). Syntheses of laudanosine have been effected by Pictet and Mdlle. Finkelstein (Compt. rend. 1909, 148, 925), and by Gadamer (Arch. Pharm. 1911, 249, 680; *cf.* Pschorr, Ber. 1904, 37, 1926), so that the constitution of the alkaloid is now clearly established—


Laudanosine.

Oxynarcotin $C_{22}H_{23}O_8N$, separated by Beckett and Wright (Chem. Soc. Trans. 1876, 29, 461) from impure narceine. It differs from narcotine in yielding cotarnine and hemipinic acid instead of cotarnine and opianic acid, on oxidation with ferric chloride.

Laudanine $C_{20}H_{25}O_4N$. Hesse (J. pr. Chem 1902, [ii.] 65, 42) states that this base contains three methoxyl and one hydroxyl groups, and yields a mixture of laudanine methiodide and *r*-laudanosine on treatment with methyl iodide. Gives trimetric prisms, m.p. 166° from alcohol; optically inactive.

iso-**Laudanine** is isomeric with laudanine, and was prepared by Pictet and Kramers (Arch. Sci. phys. nat. 1903, [iv.] 15, 121) by reduction of trimethylpapaveroline methochloride with tin and hydrochloric acid, m.p. 76°.

Laudanidine $C_{20}H_{25}O_4N$ *is also isomeric* with laudanine, which it closely resembles (Hesse, Annalen, 1894, 282, 209); it is separated therefrom by fractionation of the mixed hydrochlorides and is probably *l*-laudanine. It melts at 177°, and has $[\alpha]_D-87·8$ in chloroform.

Codamine $C_{20}H_{25}O_4N$, hexagonal prisms, m.p. 121° from ether. This alkaloid is strongly alkaline, contains two methoxyl and one hydroxyl groups, is soluble in alkalis and its salts are amorphous.

Pseudopapaverine $C_{21}H_{21}O_4N$, separated by

Hesse (J. pr. Chem. 1903, [ii.] 68, 190) from commercial papaverine, than which it is much more soluble in cold dry alcohol.

Papaveramine $C_{21}H_{25}O_6N$ was also obtained in a similar manner by Hesse (*ibid.*). Colourless prisms, m.p. 128°–129°.

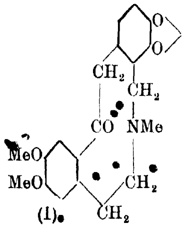
Protopapaverine $C_{19}H_{19}O_4N$, likewise isolated by Hesse (*ibid.*). Yellow leaflets, m.p. 260° (decomp.), sparingly soluble in alcohol.

Meconidine $C_{21}H_{23}O_4N$, according to Hesse (Annalen, 1870, 153, 53), may be fractionated from the mixed opium alkaloids which remain after the separation of morphine, codeine, thebaine, narcotine, and papaverine. It has m.p. 58°, and is readily soluble in alcohol or caustic soda solution.

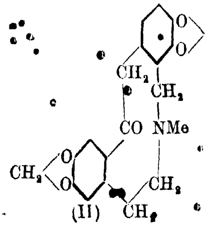
Lanthopine $C_{23}H_{25}O_4N$, m.p. 200°, similarly obtained by Hesse (*ibid.*). It is sparingly soluble in chloroform and insoluble in alkalis.

Protopine $C_{20}H_{19}O_5N$ is also known as *Macleyine*, and although first isolated by Hesse from opium is also found in other plants such as *Macleya cordata, Chelidonium majus*, etc. It separates from chloroform and alcohol as monoclinic crystals, m.p. 208°.

Cryptopine $C_{21}H_{23}O_5N$ was discovered by T. and H. Smith (Pharm. J. 1867, 27, 595, 716), and crystallises from alcohol in prisms, m.p. 218°. The salts form jellies which gradually crystallise on long standing. W. H. Perkin, jun. (Chem. Soc. Trans. 1916, 109, 815; 1919, 115, 713), in an exhaustive investigation deduced the subjoined constitutional formula for cryptopine (I) and protopine (II):—



(I)



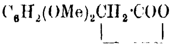
(II)

Tritopine $C_{42}H_{54}O_7N_2$, fractionated from admixture with the two foregoing alkaloids by Kauder (Arch. Pharm. 1890, 228, 119). Gives needle-like plates, m.p. 182°, from alcohol; it is di-acidic and forms a very soluble acid oxalate.

Rheadine $C_{21}H_{21}O_6N$ only occurs in very minute proportion in opium, and was obtained by Hesse (Annalen, 1864–5, Suppl. 4, 50; 1866, 140, 145; 1869, 149, 35) from *Papaver Rhœas*. It crystallises in colourless prisms, m.p. 232° (decomp.), 245°–247° according to Pavesi (Chem. Soc. Abst. 1906, [ii.] 483). When treated with strong acids, is converted into *Rheagenine*, rectangular leaflets, m.p. 223°, or 235°–237° (Pavesi).

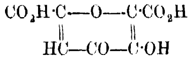
Hydroxycodeine (*Neopine*) $C_{18}H_{21}O_4N$ was separated by T. and H. Smith in the form of hydrobromide from final opium mother liquids. Dobbie and Lauder (Chem. Soc. Trans. 1911, 99, 34) showed that it contained one methoxyl group and was a tertiary base. Its colour reactions and absorption spectrum are similar to those of codeine, with which it may be closely related; but it is not identical with Ach and Knorr's (Ber. 1903, 36, 3067) hydroxycodeine.

In addition to the foregoing alkaloids, opium contains also certain neutral compounds. These are: **Meconin**, $C_{10}H_{10}O_4$, discovered by Dublanc (Ann. Chim. [ii.] 49, 5), but more completely studied by Couerbe (Annalen, 5, 180); it is also produced, together with hydrocotarnine, by the reduction of narcotine. Meconin crystallises from water in prisms, m.p. 102°, and combines with alkalis to form salts of meconinic acid, of which it is the lactone: its constitution is represented by the formula—



$$C_6H_2(OMe)_2\underbrace{CH_2\cdot COO}$$

(Hessert, Ber. 11, 257). **Meconoisin** $C_8H_{10}O_2$ was isolated by T. and H. Smith in the mother liquor from the preparation of meconin; it is crystalline and has m.p. 88° (Pharm. J. [iii.] 8, 981). Opium also contains from 3 to 5 p.c. of a characteristic acid, **Meconic** acid $C_7H_4O_7,3H_2O$, hitherto regarded as the trihydrate of 3-hydroxy-4-pyrone-2:6-dicarboxylic acid—



$$\begin{array}{c}CO_2H\cdot C\text{—}O\text{—}C\cdot CO_2H\\ \|\qquad\qquad\| \\ HC\text{—}CO\text{—}C\cdot OH\end{array}$$

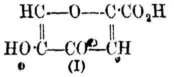
but it has recently been shown (W. Borsche, Ber. 1916, 49, 2538) that on reduction with hydrogen in presence of colloidal palladium this body yields $\alpha\beta\gamma\epsilon$-tetrahydroxypimelic acid

$$CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CO_2H$$

from which the conclusion is drawn that meconic acid is not a pyrone derivative but is really an open-chain compound of the constitution

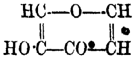
$$CO_2H\cdot C(OH)_2\cdot CH(OH)\cdot CO\cdot CH_2\cdot C(OH)_2\cdot CO_2H$$

This view, however, should be accepted with reserve, since it is at variance with experience as to the possibility of two hydroxyl radicles being attached to a single carbon atom. At 100° meconic acid loses its water of crystallisation, and between 120° and 200° it breaks up into carbon dioxide and *comenic acid*, $C_6H_4O_5$, (I), while at still higher temperatures a further molecule of carbon dioxide is removed and *pyromeconic acid*, $C_5H_4O_3$, (II) remains



$$\begin{array}{c}HC\text{—}O\text{—}C\cdot CO_2H\\ \|\qquad\qquad\| \\ HO\cdot C\text{—}CO\text{—}CH\end{array}$$

(I)



$$\begin{array}{c}HC\text{—}O\text{—}CH\\ \|\qquad\qquad\| \\ HO\cdot C\text{—}CO\text{—}CH\end{array}$$

(II)

Borsche (*ibid.*) demonstrated that when these two bodies are reduced, the pyrone bridge is not broken and the end-products of the reaction are pentamethylene oxide derivatives. Hence it would appear that they can hardly be regarded as constituted analogously to meconic acid. **Thebolactic** acid of T. and H. Smith (Pharm. J. [ii.] 7, 50) has been shown by Stenhouse and Buchanan to be identical with lactic acid, but it is possibly not an original constituent of the poppy-juice.

The less important constituents of opium represent 75 p.c. of its weight. Water varies from 10 p.c. in Persian, 12½ p.c. in Benares, to 30 p.c. in certain kinds of Turkey opium. About 40 or 50 p.c. of opium consists of indefinite gummy matter together with *pectin, albumin* and insoluble debris, the last consisting of fragments of capsules, wax, caoutchouc, calcium salts, &c. Hesse states (Ber. 3, 637) that the wax is a mixture of cerotyl palmitate and cerotyl cerotate. On ignition, opium leaves 4 to 8 p.c. of ash consisting chiefly of sulphate and phosphate of calcium and magnesium. Poppy juice contains no starch or tannin, so that the presence of these bodies in opium may indicate adulteration. (For further information on the opium alkaloids, reference may be made to Henry The Plant Alkaloids, J. and A. Churchill.)

H. E. W.

OPOBALSAM *v.* Oleo-resins.

OPODELDOC. *Linimentum Saponato-camphoratum.* A solution of soap, camphor, and volatile oils in alcohol, used externally in rheumatism, sprains, &c.

OPOPANAX or **OPOPONAX** *v.* Gum-resins.

OPTOCHIN. Syn. for Ethylhydrocupreine.

ORANGE. *Citrus Aurantium* (Linn.).

Many varieties are known, differing in size, shape, colour, flavour, and other respects. König gives as the average of a very large number of determinations—

Mean wt. of fruit. in grams.	Percentage proportion of— Rind	Flesh	Pips
188·4	27·8	71·0	1·2

The flesh contains—

Water	Protein	Invert sugar	Cane sugar	Citric acid	Ash
84·3	1·1	2·8	2·9	1·4	0·4

The juice contains—

Total extract	Invert sugar	Cane sugar	Citric acid	Protein	Ash
13·0	4·1	5·0	1·4	0·4	0·3

The following figures were obtained by Farnsteiner and Stüber (Zeitsch. Nahr. Genussm. 1904, 8, 603) from the examination of the juice of Valencia and Messina oranges:—

	Valencia oranges	Messina oranges
Sp.gr. at 15° . .	1·0464	1·0451
„ „ after boiling	1·0466	1·0455
Grams per 100 c.c.—		
Total solids, dried at 100°	10·92	10·85
Citric acid (anhydrous) .	1·79	1·47
Total sugar (as invert sugar) . . .	7·65	7·86
Ash	0·52	0·52
Nitrogen . . .	0·099	0·075
Polarisation in 200 mm. tube, direct . .	−0·11°	+2·45°
Polarisation in 200 mm. tube, after inversion .	−3·16°	−3·66°

When oranges, cut in halves, are kept under sterile conditions they undergo a slight loss in weight, which is accompanied by a marked loss in acidity and a slighter diminution in sugar together with inversion of some of the sucrose. These changes are not entirely due to oxidation, as they proceed to a less extent in a vacuum. It is probable that there is also some diastatic action (André, Compt. rend. 1921, 174, 1399; Abstracts Chem. Soc. 1922, [i.] 209).

The characteristic flavour of oranges is due to the sugar, free citric and malic acids, and essential oil which they contain. The last-mentioned is most abundant in the rind (*v.* Oils, essential). The non-protein nitrogenous matter of oranges consists chiefly of asparagine and glutamine (Scurti and de Plato, Chem. Zentr. 1908, ii. 16, 1370).

The fibrous, insoluble, inside portions of Japanese oranges were found to contain—

Water	Protein	Fat	Galactan	Pentosan	Cellulose	Ash
12·16	5·27	1·28	18·91	27·72	32·51	2·15

(Bahadur, Bull. Coll. Agr. Tokyo Imp. Univ. 1906, 7, 121). The leaves of the bitter orange (*Citrus vulgaris* [Risso]) contain stachydrine (Jahns, Ber. 1896, 29, 2065). Dried orange-peel, softened with acetic acid and boiled with water, yields about 8 or 9 p.c. of lævulose (Bauer, Landw. Versuchs-stat. 1894, 45, 298). H. I.

ORANGITE. An orange-coloured variety of the mineral thorite (*q.v.*), occurring as tetragonal crystals and irregular masses, occasionally a few ounces in weight, in the augitesyenite of southern Norway. It was described and named by C. Bergemann in 1851, and believed by him to contain a new element 'donarium.' The identity of the mineral with thorite has long been recognised. L. J. S.

ORANGE, CHROME, *v.* Chromium.

ORANGE, CROCEÏN, *v.* Azo- colouring matters.

ORANGE FLOWERS, OIL OF, *v.* Oils, essential.

ORANGE, GOLD, *v.* Azo- colouring matters.

ORANGE LEAVES, OIL OF, *v.* Oils, essential.

ORANGE M; ORANGE, MANDARIN; ORANGE, METHYL; ORANGE, NAPHTHOL, *v.* Azo- colouring matters.

ORANGE OCHRE. *Burnt Roman ochre* *v.* Pigments.

ORANGE OIL *v.* Oils, essential.

ORANGE, PALATINE, *v.* Palatine orange

ORANGE RUSSET. *Rubens madder v.* Pigments.

ORANGE, SALICYLIC, *v.* Salicylic acid.

ORANGE YELLOW *v.* Azo- colouring matters.

ORCEÏN *v. Orcinol,* art. Phenol and its homologues.

ORCHELLA WEED *v.* Archil.

ORCHIDIN *v.* Synthetic drugs.

ORCHIL *v.* Archil.

ORCHIL SUBSTITUTE *v.* Azo- colouring matters.

ORCHIPIN *v.* Synthetic drugs.

ORCIN *v. Orcinol,* art. Phenol and its homologues.

ORCINOL *v.* Phenol and its homologues.

ORDEAL BEAN. *Calabar Bean, Physostigmatis semina,* B. P., *Physostigma,* U.S. P., *Eseré Nut* (*Fève de Calabar,* Fr.; *Kalabarbohne,* Ger.). The seeds of the *Physostigma venenosum* (Balfour), a climbing plant, inhabiting the banks of the Niger and Old Calabar rivers near their mouths, in Western Africa (*cf.* Bentl. a. Trim. 80, and, for an allied species, Holmes, Pharm. J. [iii.] 9, 912). The plant has a woody stem, and ascends to a height of fifty feet. The seeds are exceedingly poisonous, a property known to the natives in the neighbourhood of the Gulf of Guinea, by whom they are administered as an ordeal to be undergone in cases of suspected witchcraft. Daniel, about 1840, introduced ordeal bean into Europe (N. Ed. Pharm. J. 40, 313).

Physostigmine (*eserine*) $C_{15}H_{21}O_2N_3$ is the principal physiologically active constituent; this alkaloid acts on plain muscle and glands like pilocarpine and similarly antagonises atropine (*v. e.g.* Cushny, J. Physiol. 1910, 41, 233). Thus physostigmine causes contraction of the pupil, whence its use in ophthalmic medicine. It is also given in tetanus, in strychnine poisoning, and in veterinary practice as a hypodermic purgative. Although very poisonous, the alkaloid is tasteless.

Physostigmine is extracted from the powdered seeds by hot alcohol and the alcohol is distilled off. The residue is mixed with sodium carbonate and repeatedly extracted with ether; the ether is shaken with 5 p.c. sulphuric acid in successive portions until the aqueous solution is just acid. The neutral solution of the sulphate so obtained crystallises on evaporation (Petit, J. Pharm. Chim. [iv.] 14, 255), but as the sulphate is very soluble, it is better to add a concentrated solution of sodium salicylate, when physostigmine salicylate separates as a crystalline powder (Salway, Chem. Soc. Trans. 1911, 99, 2150). From the salts the free base is obtained by shaking with ether and sodium carbonate, and is crystallised from benzene and light petroleum (Jobst and Hesse, Annalen, 1864, 129, 115; Vée, J. 1865, 456; Hesse, Annalen, 1867, 141, 82; Petit and Polonowski, Bull. Soc. chim. 1893, [iii.] 9, 1008; Orloff, Chem. Zeit. 1897, 1214; Salway, *l.c.*).

Salts.—The *sulphate* is the only salt official in the B. P., the *salicylate* now the only one in the U.S. P. The former, $B_2{\cdot}H_2SO_4,xH_2O$, forms colourless needles, m.p. 150°–151°, very soluble in water, alcohol, or chloroform, less so in ether (1 in 200 at 25°). The salicylate $B{\cdot}C_7H_6O_3$ forms acicular crystals, m.p 182°–183°; 1 gram dissolves in 75 c.c. of water, in 16 c.c. of alcohol, in 6 c.c. of chloroform, and in 250 c.c. of ether at 25°, also in 16 c.c. of water at 80° and 5 c.c. of boiling alcohol (U.S. P.). The *benzoate* $B{\cdot}C_7H_6O_2$, m.p. 115°–116°, dissolves in 4 parts of cold water; the *picrate* melts at 114°, and the *mercuri-iodide* $B{\cdot}HI,HgI_2$, crystallised from alcohol, melts at 70°. No definite aurichloride or platinichloride is known.

Properties.—Physostigmine is dimorphous (Salway) forming unstable crystals, m.p. 86°–87°, and more stable ones, m.p. 105°–106°; $[a]_D = -75{\cdot}8°$ to $-82°$ in chloroform, $-120°$ in benzene. It is only very slightly soluble in water, giving a solution strongly alkaline to litmus. On exposure to air, particularly when moist and in the presence of alkalis, the alkaloid changes first to *rubreserine* $C_{13}H_{16}O_2N_2$, red needles. By evaporating with ammonia on the water-bath it becomes red, green, and finally a true dye, *eserine-blue*, is formed (Ehrenberg, Verh. Ges. deut. Naturf. Aerzte, 1893, [ii.] 102), which, according to Salway (Chem. Soc. Trans. 1912, 101, 986), has the composition $C_{17}H_{23}O_2N_3$. A crystal of the alkaloid dissolved in a drop of fuming nitric acid and evaporated to dryness at 100° leaves a green residue. Similar colour reactions take place with bromine water, molybdic acid, titanium oxide, etc. (*v.* Reichard, Pharm. Zentral-Halle, 1909, 50, 375). Alkalis in the absence of air and strong acids hydrolyse eserine to a phenolic base *eseroline* $C_{13}H_{18}ON_2$, m.p. 129°, $[a]_D = -107°$ (from which rubreserine is derived by oxidation). The other products of the hydrolysis are carbon dioxide and methylamine, and conversely eseroline is reconverted in ethereal solution by methyl carbimide and a trace of sodium to eserine (Polonovski and Nitzberg, Bull. Soc. chim. 1916, [iv.] 19, 27)

$$(C_{13}H_{17}N_2)OH + CH_3{\cdot}NCO = (C_{13}H_{17}N_2)OOC{\cdot}NH{\cdot}CH_3$$

Eserine is therefore the methylurethane of a phenol. The corresponding phenylurethane (*pheneserine*) and various other derivatives have been prepared by Polonowski (Bull. Soc. chim. 1916, [iv.] 19, 46). The constitution of eserine has been further investigated by Salway (Chem. Soc. Trans. 1912, 101, 978), who obtained by zinc-dust distillation 2-methylindole and a little 1-methylindole, and by Straus (Annalen, 1913, 401, 350; 1914, 406, 332), who distilled methyleserolinium carbonate in a high vacuum and obtained *physostigmol* $C_{10}H_{11}ON$, m.p. 103°, apparently a Bz-hydroxy-Pr-dimethyl indole. One of the methyl groups is attached to the nitrogen atom; instead of the other a vinyl group was to be expected, so that the Hofmann degradation does not proceed normally and we remain in ignorance about one carbon atom. Eseroline, according to Straus, has two N-methyl groups, and since in its formation from eserine methylamine is split off, all three nitrogen atoms of the original alkaloid have a methyl group attached. For further work on the constitution, *cf.* Stedman (Chem. Soc. Trans. 1921, 119, 891).

Other alkaloids have been isolated from *Physostigma* seeds only in small quantities; they are apparently more or less closely related to eserine. *Geneserine* $C_{15}H_{21}O_3N_3$, m.p. 128°–129°, was extracted by Polonovski and Nitzberg (Bull. Soc. chim. 1915, [iv.] 17, 244) with ether, after soaking the drug in 2 p.c. sodium hydroxide; they obtained as much as 0·1 p.c. This alkaloid contains one oxygen atom more than eserine, to which it is reduced by zinc-dust and acetic acid, and by sulphurous acid. Geneserine has no myotic action, and gives a series of derivatives, containing one oxygen atom more than the corresponding eserine derivatives, *e.g.* with alkalis *geneseroline* $C_{13}H_{18}O_2N_2$. It is remarkable that such a relatively abundant base has not been observed before; its discoverers reject the suggestion that it is formed from eserine during extraction.

Physovenine $C_{14}H_{18}O_3N_2$, m.p. 123°, was found by Salway in minute quantity; it may be written $(C_{13}H_{17}N_2)OOCOH$, and is therefore the hydrogen carbonate of the phenol eseroline, and an intermediate stage in the hydrolysis of eserine. It is powerfully myotic and a very feeble base. Whether it is present as such in the seeds does not seem absolutely certain, as Salway submitted his extract to steam distillation. *Eseramine* $C_{16}H_{25}O_3N_4$, m.p. 238°–240°, was found by Ehrenberg (*l.c.*) and by Salway (m.p. 245°), but the amount present is so minute that the latter did not obtain enough for analysis. *Eseridine* $C_{15}H_{23}O_3N_3$, m.p. 132°, is said to be a constituent of calabar beans (Boehringer und Söhne, Pharm. Post, 1888, 21, 663), and was also obtained by Eber (Pharm. Zeit. 1892, 37, 483) by the action of sulphurous acid on eserine, which reagent would, however, hardly cause the simple hydration implied by the above formula. (The composition and melting point of eseridine approximate closely to those of geneserine given above.) Eseridine has been proposed as a substitute for eserine on account of its milder action; the chief drawback is a greater effect on the heart. The substance is neutral to litmus, and becomes yellow and dirty green with alkalis, but not red. With aqueous potassium iodate a brownish-red colouring matter is formed, and in the presence of acetic acid iodine is liberated. *Isophysostigmine* (Ogui, Apoth. Zeit. 1904, 19, 981) and *calabarine* (Harnack and Witkowski, Arch. exp. Path. Pharm. 1876, 5, 401) are very doubtful constituents of the beans. The latter seems to be a mixture of decomposition products of eserine by alkalis, with a strychnine-like action, antagonistic to that of physostigmine.

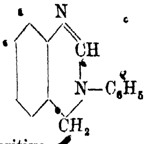
Amount and estimation of alkaloids in Calabar beans.—Carr and Reynolds (Pharm. J. 1908, [iv.] 26, 542) found a great variation in the alkaloidal content of commercial specimens of the drug, namely, between 0·04 and 0·27 p.c.; the U.S. P. demands a minimum of 0·15 p.c. The volumetric method of estimation of the U.S. P. has been criticised by Salway as giving much too low results, and he has recommended the following process (Amer. J. Pharm. 1912, 84, 49): 20 grams of Calabar beans in No. 60 powder are macerated with 200 c.c. of ether and 10 c.c. of 10 p.c. sodium carbonate solution during 4 hours. 100 c.c. of ether are withdrawn and the alkaloids extracted by shaking with several portions of N/10 acid. The combined acid liquids are made alkaline with 10 p.c. sodium carbonate solution, and the alkaloid extracted by shaking at least ten times with ether, using 20 c.c. ether each time. The combined ethereal solutions are shaken once with 5 c.c. of water, and the residue left on distilling off the ether dissolved in 5 c.c. N/10 acid and titrated back with N/50 alkali, using iodoeosin as indicator.

Non-alkaloidal constituents of the seeds are: *sitosterol* $C_{27}H_{46}O$, m.p. 136°–137°, which also occurs in germinating wheat and other plants, and *stigmasterol* $C_{30}H_{48}O,H_2O$, m.p. 170°, which is peculiar to *Physostigma.* These two sterols crystallise together (Windaus and Hauth, Ber. 1906, 39, 4378). *Calabarol* $C_{23}H_{38}O_4$, m.p. 245°, and *trifolianol* $C_{21}H_{38}O_4$, m.p. 295° (the latter also in red clover), are dihydric alcohols, found by Salway. G. B.

OREIDE. An alloy of a brilliant-yellow colour, resembling gold, made by taking copper 100, zinc 17, magnesia 6, sal ammoniac 3·6, lime 1·80, and tartar 9. The copper is melted and the other materials are added in small portions at a time, and the fused mass is skimmed and kept melted for about half an hour. The alloy has a fine grain, is malleable, takes a most brilliant polish, and if it tarnishes its lustre is restored by acidulated water.

ORELLIN. A yellow colouring matter contained in annatto, which is derived from the fruit capsules of *Bixa Orellana* (Linn.). Soluble in water and alcohol.

OREXIN. Phenyldihydroquinazoline



used as an aperitive.

ORICHALCUM. A form of brass in use among the ancient Greeks and Romans.

ORIDINE. An alkaloidal substance discovered by Hofmeister in rice polishings which showed antineuritic activity, becoming inactive on purification. Said to be isomeric with betaine and valine, and to be related to the pyridine and piperidine groups.

ORIENTAL ALABASTER *v.* ONYX-MARBLE.

ORIENTAL EMERALD, ORIENTAL TOPAZ *v.* CORUNDUM.

ORIGANUM OIL *v.* OILS, ESSENTIAL.

ORIOL YELLOW *v.* PRIMULINE AND ITS DERIVATIVES.

ORIZABA JALAP ROOT *v.* RESINS.

ORMOLU *v.* MOSAIC GOLD.

ORMOSINE, ORMOSININE. Isomeric alkaloids found in *Ormosia dasycarpa* (Jacks), a leguminous plant growing in Venezuela. For method of isolation, *see* Hess and Merck, Ber. 1919, 52 [B], 1976.

Ormosine $C_{20}H_{33}N_3,4H_2O$, long needles, m.p. 85°–87°, readily soluble in alcohol or chloroform. **Ormosinine** $C_{20}H_{33}N_3$, anhydrous cubes or short prisms, m.p. 203°–205°, sparingly soluble in alcohol. For description of their salts, *see* Hess and Merck (*l.c.*).

ORNITHINE, *αδ-diaminovaleric acid*

$$NH_2[CH_2]_3CH(NH_2)CO_2H$$

was first prepared by Jaffé (Ber. 1877, 10, 1926; 1878, 11, 40) from its dibenzoyl derivative *ornithuric acid,* found in the excrement of birds that had been fed with benzoic acid. It occurs among the products of alkali hydrolysis of certain proteins, probably arising from arginine by a further hydrolysis (Kossel and Weiss, Zeitsch. physiol. Chem. 1909, 59, 492; 60, 311; 1910, 68, 160); and it can also be obtained from arginine by the action of *arginase* (*q.v.*); or by hydrolysis with barium hydroxide (Schulze and Winterstein, Ber. 1897, 30, 2879; Kiesel, Zeitsch. physiol. Chem. 1911, 75, 169).

Jaffé (*l.c.*) showed that ornithine was a diaminovaleric acid, the position of the two amino groups being determined by Ellinger (Ber. 1898, 31, 3183), who obtained *putrescine* (tetramethylenediamine, Udransky and Baumann, *ibid.* 1888, 21, 2938) and carbon dioxide by the action of putrefying pancreas on ornithine.

$$\underset{\text{Ornithuric acid.}}{COPh\cdot NH[CH_2]_3CH(NH\cdot COPh)CO_2H}\cdot$$

$$\rightarrow \underset{\text{Ornithine.}}{NH_2[CH_2]_3CH(NH_2)CO_2H} \rightarrow \underset{\text{Putrescine.}}{NH_2[CH_2]_4NH_2}$$

Ornithine has been synthesised by Fischer (Ber. 1901, 24, 454) by the following series of reactions:—

Ethyl-γ-phthalimidopropylmalonate

$$C_6H_4[CO]_2N\cdot[CH_2]_3\cdot CH(CO_2Et)_2$$

obtained from potassium phthalimide, propylene bromide, and ethyl sodiomalonate, yields ethyl γ-phthalimidopropylbromomalonate on bromination; this is converted by hydrolysis with loss of carbon dioxide into δ-phthalimido-α-bromovaleric acid $C_6H_4[CO]_2N[CH_2]_3CHBr(CO_2H)$, which, on treatment with ammonia and subsequent hydrolysis, yields αδ-diaminovaleric acid or inactive ornithine. A similar synthesis has been effected by Sörensen (Zeitsch. physiol. Chem. 1905, 44, 448); and a synthesis from benzoylpiperidine is described by Fischer and Zemplén (Ber. 1909, 42, 1022).

For the intermediary metabolism of ornithine in the organism, *v.* Ringer, Frankel and Jonas (J. Biol. Chem. 1913, 14, 545).

dl-Ornithine has been obtained in crystalline form (Fischer and Bergmann, Annalen, 1913 398, 109); it is readily soluble in water, forming an alkaline solution; it contains an asymmetric carbon atom and derivatives of the dextro-, lævo-, and racemic varieties are described.

d-**Ornithine**, The ornithine hydrochloride obtained by hydrolysis of naturally occurring ornithuric acid has $[\alpha]_D+15{\cdot}64°$ to $16{\cdot}8°$ (Schulze and Winterstein, Zeitsch. physiol. Chem. 1901, 34, 128), and *d*-ornithine is also obtained by the hydrolysis of *d*-arginine with barium hydroxide.

Salts.—Hydrochlorides $C_5H_{12}O_2N_2,2HCl$ and $C_5H_{12}O_2N_2,HCl$; platinichloride

$$C_5H_{12}O_2N_2,H_2PtCl_6;$$

nitrate $C_5H_{12}O_2N_2,HNO_3$;
oxalate $3C_5H_{12}O_2N_2,2C_2H_2O_4$;
acetate, m.p. 161°–162°;
picrate $C_5H_{12}O_2N_2,C_6H_3O_7N_3$

(Schulze and Winterstein, *l.c.*); crystallises with $1H_2O$, and has m.p. 203°–204° (Kossel and Weiss, Zeitsch. physiol. Chem. 1910, 68, 160).

Acyl derivatives.—The hydantoin C[illegible]$H_{20}O_3N_4$, m.p. 191°–192°; the β-naphthalenesulphone

$$C_5H_{10}O_2N_2(SO_2{\cdot}C_{10}H_7)_2$$

m.p. 189° (Riesser, Zeitsch. physiol. Chem. 1906, 49. 210); the monobenzoyl $C_{12}H_{16}O_3N_2$, m.p. 225°–240°; the dibenzoyl (*d-ornithuric acid*)

$$PhCO{\cdot}NH[CH_2]_3CH(CO_2H)NH{\cdot}COPh$$

m.p. 184°–185°, $[\alpha]_D+9{\cdot}2°$ to $9{\cdot}3°$ in 10 p.c. solution of sodium salt, $+8{\cdot}5°$ in 20 p.c. solution; brucine *d*-ornithurate

$$C_{19}H_{20}O_4N_2{\cdot}C_{23}H_{26}O_4N_2,H_2O$$

m.p. 135°–136°, separates from a solution of brucine in racemic ornithuric acid.

l-**Ornithine.** *Acyl derivatives.*—The dibenzoyl (*l*-ornithuric acid) $C_{19}H_{20}O_4N_2$, from *dl*-ornithuric acid by fractional crystallisation of the cinchonine salt; m.p. 188°–189°, $[\alpha]_D-9{\cdot}22°$ in 10 p.c. solution of the sodium salt; cinchonine *l*-ornithurate $C_{19}H_{20}O_4N_2{\cdot}C_{19}H_{22}ON_2,H_2O$, the anhydrous salt has m.p. 154°–155° (corr.); the monobenzoyl $C_{12}H_{16}O_3N_2$, m.p. 240°; the phenyl*iso*cyanate, m.p. 189°–190° (corr.); the hydantoin, m.p. 191° (corr.).

dl-**Ornithine**, obtained by the putrefactive hydrolysis of arginine carbonate (Ackermann, Zeitsch. physiol. Chem. 1908, 56, 305; *cf.* Neuburg, Biochem. Zeitsch. 1911, 37, 507); by hydrolysis of clupeine sulphate with barium hydroxide (Kossel and Weiss, *ibid.* 1909, 59, 492; 60, 311); is also prepared by any of the synthetic methods described above.

Salts.—Hydrochloride $C_5H_{12}O_2N_2,HCl$, m.p. 215°; aurichloride $C_5H_{12}O_2N_2(HAuCl_4)_2,H_2O$, decomposes at 173°–175°; platinichloride $C_5H_{12}O_2N_2.H_2PtCl_6$; sulphate

$$(C_5H_{12}O_2N_2)_2H_2SO_4$$

m.p. 213°; nitrate $C_5H_{12}O_2N_2{\cdot}HNO_3$, m.p. 183°; oxalate $(C_5H_{12}O_2N_2)_2C_2H_2O_4$, m.p. 218°; carbonate; acetate $C_5H_{12}O_2N_2{\cdot}C_2H_4O_2$, m.p. 163°–164°; monopicrate $C_5H_{12}O_2N_2{\cdot}C_6H_3O_7N_3$, m.p. 195°, triclinic system

$$a:b:c=0{\cdot}6962:1:0{\cdot}6301$$

$\alpha=93°\ 10'$, $\beta=100°\ 55'$, $\gamma=81°\ 19'$; dipicrate, $C_5H_{12}O_2N_2(C_6H_3O_7N_3)_2,2\tfrac{1}{2}H_2O$, m.p. 183°–184°; picrolonate $C_5H_{12}O_2N_2{\cdot}C_{10}H_8O_5N_4{\cdot}1\tfrac{1}{2}H_2O$, m.p. 220°–221°. *Double salts*, with cupric sulphate $(C_5H_{12}O_2N_2)_2CuSO_4,H_2O$, m.p. 204°–205°; with cupric nitrate $(C_5H_{12}O_2N_2)_2Cu(NO_3)_2,\tfrac{1}{2}H_2O$, m.p. 167°–168°; with silver nitrate

$$C_5H_{12}O_2N_2{\cdot}HNO_3,AgNO_3$$

m.p. 175°, v. Weiss (Zeitsch. physiol. Chem. 1909, 59, 499); *v.* for the separation of ornithine as picrate from other bases v. Kossel and Weiss (Zeitsch. physiol. Chem. 1910, 68, 160).

Acyl derivatives.—The phenyl*iso*cyanate, m.p. 192°; the hydantoin, m.p. 194°–195°; the β-naphthalenesulphone $C_5H_{10}O_2N_2(C_{10}H_7SO_2)$, m.p. 195°–196°; the δ-monobenzoyl

$$PhCO{\cdot}NH[CH_2]_3CH(NH_2)CO_2H$$

m.p. 260°, or 285°–288°, on the Maquenne block. The δ-*m*-nitrobenzoyl $C_{12}H_{15}O_5N_3$, m.p. 250°; the α-monobenzoyl

$$NH_2[CH_2]_3CH(NH{\cdot}COPh)CO_2H$$

m.p. 264°–267°, on the Maquenne block; the γ-hydroxy-α-benzoyl, m.p. 255°–256° (Hammarsten, Compt. rend. Lab. Carlsberg, 1916, 11, 223); and the αδ-dibenzoyl (*dl*-ornithuric acid) $C_{19}H_{20}O_4N_2$, m.p. 187°–188°.

αδ-Dimethylaminovaleric acid

$$MeNH[CH_2]_3CH(NHMe)COOH$$

forms microscopic six-sided plates; the chloroplatinate crystallises in yellowish-red clusters, m.p. 216° (decomp.). For γ-hydroxyornithine (αδ-diamino-γ-hydroxyvaleric acid) *v.* Sörensen (Compt. rend. trav. lab. Carlsberg, 1916, 11, 223).

M. A. W.

ORPHOL. Bismuth β-naphtholate, *v.* BISMUTH, ORGANIC COMPOUNDS OF; *also* SYNTHETIC DRUGS.

ORPIMENT (*Auripigmentum*). Native arsenic trisulphide, As_2S_3, crystallising in the orthorhombic system and isomorphous with stibnite (Sb_2S_3). Crystals are rare, the mineral usually occurring as laminated or scaly masses with a perfect cleavage parallel to the surface of the plates. The colour is lemon-yellow, and there is a pearly lustre on the cleavage surfaces. The mineral is very soft and sectile (H. 1½–2), and the flakes are readily bent; sp.gr. 3·48. Orpiment occurs, usually in association with realgar (*q.v.*), in mineral-veins together with ores of silver, lead, &c., and also as nodules in beds of sandy clay. It is found at several places in Hungary, at Allchar in Macedonia, Mercur in Utah, and in some abundance at Julamerk in Asiatic Turkey, and Zarshuran in Persia. Some hundreds of tons are exported annually from Shih-haung-Ch'ang in prov. Yunnan, China. The mineral is used as a pigment

(King's yellow), but now mostly in the East; it is the auripigmentum (golden paint) of the ancients. Formerly it was also used in dyeing and calico-printing, and by tanners for removing hair from skins. L. J. S.

ORRIS ROOT is the peeled and dried rhizomes of *Iris florentina* (Linn.), *I. pallida* (Lam.), and *I. germanica* (Linn.). It is characterised by a pleasant aroma, and appears to be slightly detergent and antiseptic. It is employed in the preparation of violet-powder and dentifrices, and to a small extent as an ingredient of snuff.

ORSEILLINE *v.* Azo- COLOURING MATTERS.

ORSELLINIC ACID $C_8H_8O_4,H_2O$ was first prepared by Stenhouse (Annalen, 68, 61), by digesting lecanoric acid with boiling baryta water, and can also be produced from erythrin in a similar manner. According to Hesse (*ibid.* 139, 35), the solution of erythrin in baryta water is heated on the steam-bath until a sample of the product no longer yields a gelatinous precipitate when neutralised with hydrochloric acid. The liquid is then acidified, and the orsellinic acid, which separates on standing, is crystallised from alcohol or acetic acid.

Orsellinic acid crystallises from dilute acetic acid in needles with $1H_2O$. When heated, it melts at 176° with evolution of carbon dioxide and formation of orcin, and is evidently an orcin carboxylic acid.

Ethyl orsellinate $C_{10}H_{12}O_4$, colourless leaflets, m.p. 132°, is produced when erythrin is boiled for several hours with alcohol (Stenhouse, *l.c.*), and can be prepared in an identical manner from lecanoric acid (Schunck, Annalen, 54, 265).

Methyl orsellinate $C_9H_{10}O_4$ (Schunck, *l.c.*, and Stenhouse, *l.c.*), and iso*amyl orsellinate* $C_{13}H_{18}O_4$ (Stenhouse; Hesse, Annalen, 139, 37), m.p. 76°, have also been obtained.

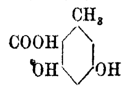
According to Heinrich (Ber. 1904, 37, 1406), ethyl orsellinate in alkaline solution reacts with diazobenzene chloride, with formation of the disazobenzene derivative

$$C_6Me(OH)_2(C_6H_5N_2)_2COOEt$$

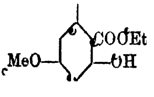
red needles, m.p. 186°, and this, on reduction with stannous chloride and hydrochloric acid, and further heating with hydrochoric acid at 160°, gives diamino-orcin hydrochloride

$$C_6HMe(OH)_2(NH_2)_2(Me:(NH_2)_2:(OH)_2=1:2:4:3:5$$

The constitution of orsellinic acid is therefore to be represented as follows:—

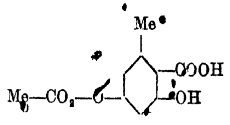


This structure is supported by the conductivity of measurements of Thiel, Schumacher, and Roemer (Ber. 1905, 38, 3860), and further by the work of Fischer and Hoesch (Annalen, 1912, 391, 347). These last authors treated methyl-orsellinate with an ethereal solution of diazomethane—which methylates phenol carboxylic acids preferentially in the para-position—and thereby obtained an *a-methyl ether*—

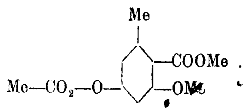


m.p. 72°–75°, which gave a red-violet ferric chloride reaction.

When orsellinic acid was treated with methylchlorocarbonate in cold N caustic soda—a reagent which also preferentially attacks the para-position—the product of the reaction was *methyl-carbonato-orsellinic acid*—

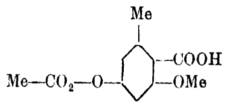


(5-methyl-carbonato-3-hydroxy-o-toluic acid), m.p. 153°–154° (corr.), which also gave a characteristic coloration with ferric chloride, whereas the product of the action of ethereal diazomethane on this last substance was *methyl-carbonato-orsellinate-β-methyl ether*—

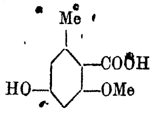


m.p. 86° (corr.), which gave no coloration with ferric chloride.

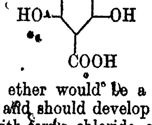
On hydrolysis of this ester with concentrated sulphuric acid at 25°, *methyl-carbonato-orsellinic-acid-β-methyl ether*—



m.p. 145° (corr.), was obtained, which also failed to develop a coloration with ferric chloride, whereas, when this was further hydrolysed by means of caustic soda, it yielded *orsellinic acid-β-methyl ether*—

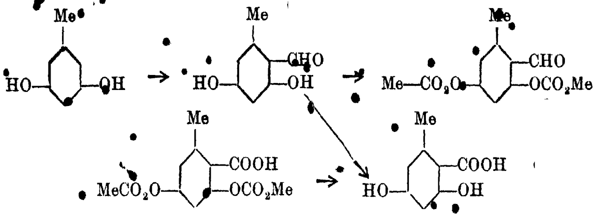


which decomposes at 175°, and develops a yellow-red coloration with ferric chloride. As Fischer and Hoesch point out, were the older formula for orsellinic acid correct—



the β-methyl ether would be a derivative of salicylic acid, and should develop its characteristic colour with ferric chloride, and moreover, the α- and β-methyl ethers would be identical, whereas they are undoubtedly isomeric.

The constitution thus arrived at has been substantiated by the synthesis of orsellinic acid by Hoesch (Ber. 1913, 46, 886), who obtained it by oxidation of orcyl-aldehyde—prepared from orcine by Gattermann's method—or, more readily, of its dimethylcarbonato, or diethylcarbonato derivatives, followed by hydrolysis of the resulting acid with N caustic soda solution. The synthesis may be represented thus—



An attempt to prepare this acid from orcinol by a method analogous to that used for the preparation of salicylic acid from phenol was unsuccessful.

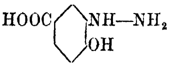
Dimethylcarbonato-orcyl aldehyde, needles, m.p. 84°–85°, according to Hoesch becomes yellow on exposure to light.

Monomethylcarbonato-orcyl aldehyde, prisms, melts at 79°, *diethylcarbonato-orcyl aldehyde*, needles, at 60°, and *diethylcarbonato-orsellinic acid*, prisms, at 112° (decomp.).

Tetra-acetyl-glucose ester of orsellinic acid, white needles, m.p. 153°. $[\alpha]_D^{18}$ $-41{\cdot}75°$ or $-41{\cdot}40°$ (in chloroform) (Karrer, Baumgarten, Günther, Harder and Lang, Helv. Chim. Acta, 1921, 4, 130). A. G. P.

ORSUDAN. Trade name for sodium acetyl-2-aminotolyl-5-arsinate (see ARSENICALS, ORGANIC).

ORTHIN. A phenylhydrazine derivative.

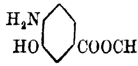


Formerly used as an antipyretic and analgesic.

ORTHITE, or Allanite. A complex rare-earth silicate belonging to the epidote group of minerals, and sometimes known as cerium-epidote. The general formula is $HR''R_3'''Si_3O_{13}$, where R''=Ca, Fe, and R'''=Al, Fe, Ce, La, Di, Y. The extreme values in the analyses tabulated by Dana are: SiO_2, 29·3–34·5; ThO_2, trace–3·5; Al_2O_3, 6·3–22·9; Fe_2O_3, 1·6–21·2; Ce_2O_3, 1·3–33·7; Di_2O_3, 2·9–24·0; La_2O_3, 0·2–8·1; Y_2O_3, 0·3–4·2; Er_2O_3, 0–2·0; H_2O, 0·3–14·6; also small amounts of manganous oxide, magnesia, and alkalis. Scandium (Sc_2O_3 1 p.c.) has been detected in orthite from Impilaks in Finland. Sp.gr. 3·5–4·2. The mineral crystallises in the monoclinic system, and has either a tabular or a long prismatic habit. Compact masses and grains are also common. It is black or dark brown, opaque, and with a pitchy lustre on the bright sub-conchoidal fracture. On the exterior the material often presents a dull weathered appearance, the slender prismatic crystals looking rather like rusty nails. Tabular crystals from Greenland were described by T. Allan in 1808, and named allanite by T. Thomson in 1810. The later name orthite (from ὀρθός, straight) was given by J. J. Berzelius in 1818 to long prismatic crystals from Finbo in Sweden. Owing to difficulties of determination and to differences in composition and degree of hydration, several other minerals, now recognised as varieties of allanite, have been described as distinct species under special names. As an accessory constituent of crystalline rocks (gneiss, granite, pegmatite, andesite, &c.), allanite is not of uncommon occurrence in small amounts. It is well known in the granite of Criffel and several other places in Scotland, and in a quartz vein traversing granophyre in Merionethshire. It is found in some abundance in the felspar quarries of Sweden and Norway, and as large masses in gneiss at several American localities. Masses weighing over 300 pounds have been found at Barringer Hill in Llano Co., Texas, where, together with gadolinite, &c., it has been quarried for the supply of rare earths used in incandescent gas-lighting. A large deposit is also worked in Amherst Co., Virginia (on American localities *v.* T. L. Watson, Bull. Geol. Soc. Amer. 1917, 28, 463). L. J. S.

ORTHOCLASE. *Potash felspar v.* FELSPAR.

ORTHOFORM. Trade name for *p*-amino-*m*-hydroxy-benzoic-methyl ester



White powder, sparingly soluble in water, non-toxic. Used as a dusting powder for painful wounds and as a local anæsthetic (*v.* SALICYLIC ACID).

ORTHOFORM, NEW, *v.* SALICYLIC ACID.

ORTOL. Trade name for a mixture of methyl-*o*-amidophenol and hydroquinone. Used as a photographic developer.

ORYZANIN. Hens, doves, mice, and other animals readily become ill when fed exclusively with shelled rice, and finally die, after a great loss of body weight. This effect is due to the absence of a substance which is essential to life, and which has been isolated from rice husks. Whenever this substance is absent from a diet, the diet is insufficient to support life. If it be added to an artificial diet of fat, protein, carbohydrate, and salt, in which it is absent, the diet again becomes efficient. Dogs also cannot live without oryzanin, and they rapidly waste when fed on shelled or extracted rice. If they receive 0·3 gram oryzanin daily when in a wasted condition produced by oryzanin-free diet, they rapidly recover. Oryzanin is fairly widely distributed in various foodstuffs.

The oryzanin is extracted from fat-free husks (previously extracted with ether) by alcohol. From the alcoholic extract it is precipitated by phosphotungstic acid. From the phosphotungstate precipitate, after the usual treatment, a still more active preparation is obtained by precipitation with tannic acid, and from this further purified substance, oryzanin is obtained in the form of a crystalline picrate. On hydrolysis with acids it yields two acids of unknown constitution, choline, dextrose, and nicotinic acid (Suzuki, Shimamura, and Odake, Biochem. Zeitsch. 1912, 43, 89). Kurono, J. Coll. Agric. Imp. Univ. Tokyo, 1915, 5, 305) found that when added to the extent of 0·01–0·1 p.c. it accelerates the growth and fermentation of yeasts in beer-wort, koji extract, and in artificial media such as Hayduck's or Nägeli's solutions, its stimulating action being much greater than that of peptone, asparagin, &c. The accelerating action of malt culms on distillery fermentations is attributed by Kurono to oryzanin.

OSAGE ORANGE TREE. The wood of this tree has been used for many years for dyeing by the Indians in the Red Valley region of Texas, America, and has engaged the attention of the United States Forest Service. As the result of its examination by Kressmann (Journ. Amer. Leather Chemists Association, 1915, 347), it has been found that its dyeing properties are very similar to those given by old fustic, the shades which it produces being, however, slightly purer and somewhat less red in tint. A qualitative study of the aqueous extract showed that the dyeing principles present consisted as in old fustic of *morin* and *maclurin*, but that the unknown red constituent present in this latter was practically absent. Though apparently the tinctorial strength of distinct samples of the osage orange wood is somewhat variable, this is probably on the average quite equal to that of old fustic, and this wood can be satisfactorily employed not only for textile but also for leather dyeing. A. G. P.

OSAZONES. A term given by E. Fischer to compounds of phenyl hydrazine with the sugars (*v.* HYDRAZONES and CARBOHYDRATES).

OSMIRIDIUM *v.* IRIDOSMINE; PLATINUM METALS.

OSMITOPSIS, OIL OF. *Osmitopsis asteriscoides* (Cass.), an aromatic plant of the order of *Compositæ*, growing in South Africa, yields a greenish-yellow oil of a burning taste and aromatic smell. Appears to be isomeric with borneol and oil of cajeput.

OSMIUM. Sym. Os. At.wt. 191·07.

This metal occurs in native platinum (*v.* PLATINUM), and especially in osmiridium. It differs from the other metals of the platinum group except ruthenium in forming a volatile tetroxide OsO_4, the so-called osmic acid, but it can be separated from ruthenium because the latter is volatile with chlorine only from alkaline solutions, while osmium is driven off also from acid ones.

The osmiridium treated as described under IRIDIUM (*v.* also *infra*) yields the osmium in the form of this tetroxide, which may be reduced in hydrochloric acid solution by zinc or mercury (Berzelius, Ann. Chim. 1929, [ii.] 40, 258); with an alkaline formate; with hydrogen; a mixture of carbon mon- and dioxides or with carbon. In the latter case, the metal is obtained in a crystalline form, whilst by the other methods it is precipitated as a bluish powder (Doebereiner, Annalen, 1835, 14, 17; Deville and Debray, Compt. rend. 1876, 82, 1077). A review of the methods of treating osmium residues is given by Gutbier (Chem. Zeit. 1913, 37, 857). For the estimation of osmium, *see also* Ruff and Bornemann (Zeitsch. anorg. Chem. 1910, 65, 429).

The metal has also been obtained by the reduction of its ammoniacal or sulphur compounds (Berzelius, *l.c.*; 1829, [ii.] 42, 191; Fremy, *ibid.* 1855, [iii.] 44, 387; Schneider, Annalen, 1867, Suppl. 5, 261).

Osmium has a sp.gr. of 22·48 (Joly) (its sp.gr., however, depends on its state of division); and melts at about 2700° (U.S. Com. Rep. 1919). It volatilises in the electric furnace, but less readily than the other platinum metals, so that it possesses special interest as being next to tantalum and tungsten the least fusible and probably the least volatile metal and as the heaviest known substance, qualities which, in conjunction with its susceptibility to oxidation, and the peculiar nature of its volatile oxide, distinguish it from the other platinum metals or indeed from all other known metals.

When heated osmium combines directly with fluorine, chlorine, sulphur, and with phosphorus. It is not attacked by hydrochloric acid unless the latter contains oxygen (Matignon, Compt. rend. 1903, 137, 1051).

Although osmium, when obtained in a finely divided state by treatment of an alloy with a solvent which removes the other metal, is easily oxidised or dissolved, it is much more refractory after ignition in an inert atmosphere. Finely divided osmium oxidises slowly at ordinary temperatures and burns freely at 400°, but the denser metal requires a higher temperature for complete oxidation. It is best rendered soluble by fusion with peroxides or with a mixture of caustic alkali and nitre.

On account of its infusibility, it has been employed for the manufacture of electric-light filaments, but by reason of its high cost and the extremely small supply, its use has been abandoned in favour of tantalum filaments or of the 'osram' filaments, which are made of tungsten wire and do not contain osmium as the name might imply.

It is stated by W. C. Heraeus, that 1 part of osmium will replace 2½ parts of iridium for hardening platinum, and that the improvement in elasticity is still greater. From 2 to 20 p.c. of osmium is recommended, the alloy being made in the absence of oxidising gases, and the presence of iron and copper being carefully avoided. The alloy has been patented (Eng. Pat. 29723, 1910).

A delicate test for osmium is given by Tschugaeff (Compt. rend. 1918, 167, 235). When a solution containing OsO_4 or $OsCl_4$ is warmed for a few minutes with thiourea and a few drops of hydrochloric acid the liquid acquires a deep red or rose colour which is sensitive to one part in 100,000. Hirsch (Chem. Zeit. 1922, 34, 390) substitutes KCNS in the cold for thiourea. The solution shaken with ether or amyl alcohol gives a blue layer if OsO_4 is present.

None of the osmium compounds is of technological interest, excepting the tetroxide and the osmates, as forming steps in the preparation of the metal, and (as regards the former) on account of a limited use in microscopy for staining pathological specimens. Colloidal osmium has been obtained by the reduction of its salts with hydrazine hydrate (Castoro, Zeitsch. anorg. Chem. 1904, 41, 131; Gutbier and Hofmeier, J. pr. Chem. 1905, [ii.] 71, 452).

For its catalytic action, *see* Lehmann, Arch. Pharm. 1913, 251, 152; Normann and Schlick, *ibid.* 1914, 252, 208. For a full account of the 'Haber' synthetic ammonia process with osmium as catalyst, *see* Haber and le Rossignol Zeitsch. Electroch. 1913, 19, 53. An aqueous solution of formaldehyde decomposes in the presence of osmium into carbon dioxide and methyl alcohol (Müller, Ber. 1921, 54, [B] 3214).

Compounds of Osmium.

Oxides.—**Osmium monoxide** OsO is a greyish-black powder formed when the corresponding sulphite is ignited with sodium carbonate in a current of carbon dioxide.

Osmium sesquioxide Os_2O_3 is obtained similarly as a black powder, or in copper-red scales by the reduction of the tetroxide. A corresponding brownish-red hydroxide is precipitated by the addition of alkalis to alkali osmochlorides.

Osmium dioxide OsO_2 is obtained similarly, and like the foregoing oxides, is feebly basic. It is bluish-black, but when prepared by heating its hydroxide in a current of carbon dioxide, it forms masses having a copper lustre. Pure OsO_2 may be obtained in a crystalline condition by heating the finely divided metal in the vapour of OsO_4. In absence of air it is very stable, but when mixed with combustible bodies it deflagrates on heating. Dried hydrated osmium dioxide has the composition $OsO_2,2H_2O$, and is gradually oxidised in air to the tetroxide (Ruff and Bornemann, Zeitsch. anorg. Chem. 1910, 65, 429).

The precipitated dioxide is colloidal and readily forms sols in water. Heated in a neutral gas half the water is lost below 120° and the rest below 200° (Ruff and Rathsburg, Ber. 1917, 50, 484). *See also* Amberger (Koll. Zeit. 1915, 17, 47).

Osmium tetroxide OsO_4, sometimes erroneously termed *osmic acid*, is prepared by heating finely-divided osmium in air or steam, or by dissolving it or the lower oxides in *aqua regia*. It may also be formed by attacking the metal with fused potassium hydroxide and nitrate: the mass is dissolved in water, precipitated with alcohol, and oxidised with chromic acid in a current of oxygen. The pure tetroxide so formed, when treated with potassium hydroxide and alcohol, forms *potassium osmate* $K_2OsO_4,2H_2O$, which separates as violet-coloured crystals (Ruff and Bornemann, *l.c.*). If no alcohol is added the solution is colourless and consists of *potassium perosmate* ($KOsO_4$) formerly known as *osmate*. This solution becomes brown on standing and on boiling loses OsO_4 and oxygen leaving the *osmate*. Osmium tetroxide forms glistening needles, which sublime readily, and give a colourless solution in water. The solution possesses a caustic taste, and is turned yellow by sulphur dioxide, then brown, green, and finally indigo-blue. When fused it boils at 100°, emitting a vapour of a powerful penetrating smell which attacks the lung and eyes, and produces inflammation of the mucous membrane. The tetroxide also acts violently on the skin, causing painful wounds (Deville and Debray, Ann. Chim. Phys. 1859, [iii.] 56, 400; Compt. rend. 1874, 78, 1509). It is readily reduced to the lower oxides. For its effect as a catalyst for oxidations, *see* Hofmann, Ber. 1912, 45, 3329. It is soluble in hydrochloric acid of sp.gr. 1·16, giving osmium tetrachloride.

Osmium trioxide OsO_3 is unknown, but the corresponding *osmic acid* H_2OsO_4 is formed, according to Moraht and Wischin (Zeitsch. anorg. Chem. 1893, 3, 153), by treating the potassium salt with nitric acid. Ruff and Bornemann (*l.c.*) state, however, that they could not obtain it. A number of its salts, the *osmates* (formerly known as *osmites*), are known.

Halides.—**Osmium fluorides.** By direct combination of the elements, Ruff and Tschirch (Ber. 1913, 46, 929) have succeeded in preparing three fluorides of osmium, OsF_4, OsF_6, and OsF_8. The last is the most volatile, and melts to a yellowish-red liquid at 34·5°C.

Osmium dichloride $OsCl_2$, a dark brown insoluble powder, may be formed by heating the trichloride at 500° under pressure, and cooling the vapour at −50°; or in small quantity by heating the metal in chlorine.

Osmium trichloride $OsCl_3$ is formed when ammonium osmichloride is heated at 350° in chlorine (Ruff and Bornemann; *see* also Moraht and Wischin, *l.c.*). It is readily soluble in water and gives rise to the double salts known as the *osmochlorides* or *chlorosmites* M_3OsCl_6.

Osmium tetrachloride $OsCl_4$ is prepared by heating osmium in a slow current of chlorine at 650°–700°, the issuing vapours being cooled in a tube wrapped in asbestos, or by dissolving the tetroxide in strong hydrochloric acid. It forms black metallic crusts, volatilises in a vacuum to a yellow vapour, and is slowly decomposed by water with formation of the dioxide and hydrochloric acid. It gives the series of salts known as the *osmichlorides* or *chlorosmates* M_2OsCl_6 (Gutbier and Maisch, Ber. 1909, 42, 4239; Gutbier and Walbinger, Ber. 1911, 44, 308). For certain derivatives of these and other similar compounds, *see* Rosenheim and Sasserath, Zeitsch. anorg. Chem. 1899, 21, 122; Wintrebert, Ann. Chim. Phys. 1903, [vii.] 28, 15.

Osmium bromides and iodides are also known.

Iodo-osmous acid $OsI_2 \cdot 2HI$ is formed when nascent hydrogen iodide reacts with an osmium compound. Its solution possesses a fine emerald-green colour, which rapidly turns red on exposure to air, but its salts are more stable and form permanent green solutions. This reaction may be employed as a test for osmium compounds and also for iodides in the presence of chlorides and bromides (Alvarez, Compt. rend. 1905, 140, 1254; Orloff, Chem. Zeit. 1907, 31, 1063).

Osmium tetrasulphide OsS_4 is an insoluble brown substance formed by passing sulphuretted hydrogen into a solution of the oxide. It is precipitated from alkaline solutions of OsO_4 by ammonium or potassium sulphides, in excess of which it is insoluble.

Osmium sulphite $OsSO_3$ and numerous complex sulphites have been prepared (Rosenheim and Sasserath, *l.c.*; Rosenheim, *ibid.*

1900, 24, 420). Osmium forms complex derivatives with ammonia and also an acid $OsNO_3H$, termed *osmiamic acid*, a number of the salts of which have been prepared (Werner and Dinklage, Ber. 1901, 34, 2698; *ibid.* 1906, 39, 499). By the action of acids on the osmiamates, *nitrilo* compounds of osmium are formed (Brizard, Ann. Chim. 1900, [vii.] 21, 311; Werner and Dinklage, *l.c.*).

Osmium nitrite $Os(NO_2)_3$ and complex nitrites and *nitroso* derivatives are also known (Wintrebert, *l.c.*; and Compt. rend. 1905, 140, 585). Osmium also forms a series of *osmocyanides* very similar to the ferrocyanides. *Osmium oxalates* have been prepared by Wintrebert (*ibid.* 1900, 131, 264). A. J. W.

OSMOPHORES. Groups or radicles which are supposed to determine, or to be concerned in forming, the characteristic smell of a substance.

OSMOSIS *v.* SOLUTION.

OSONES *v.* CARBOHYDRATES.

OSTEOLITE. *Calcium orthophosphate*, $Ca_3(PO_4)_2$ *v.* CALCIUM.

OTAVITE. A basic carbonate of cadmium (Cd 61·5 p.c.) crystallised in the rhombohedral system, and one of the few minerals containing cadmium as an essential constituent (*v.* GREENOCKITE). It forms white to reddish crystalline crusts of minute curved rhombohedra with a brilliant lustre. It is found in small amount, together with greenockite, malachite, cerussite, &c., lining cavities in the oxidation zone of the deposits of copper ore at Otavi in South-west Africa. L. J. S.

OTOBA BUTTER. The fat expressed from the fruit of *Myristica otoba*. Contains the glycerides of myristic, lauric, palmitic, and oleic acids; an essential oil consisting chiefly of sesquiterpenes and unsaponifiable matter containing otobite and *iso*-otobite. Otobite appears to contain one methoxy-group, but *iso*-otobite does not. Both give pentabromides, m.p. 190° and 191° respectively (Baughman, Jamieson and Brauns, J. Amer. Chem. Soc. 1921, 43, 199).

OTTO OF ROSES *v.* OILS, ESSENTIAL.

OUABAÏO. The poison of the Somalis. Along the whole of the west coast of Africa, especially in the country of the Somalis, occurs a tree used by the natives for the preparation of their arrow-poison, and called by them Ouabaïo. Its wood is yellowish-white, very hard and dense, odourless, but possessing a strong bitter taste. Arnaud has isolated from it (J. Soc. Chem. Ind., 1889, 211; 1888, 586) *ouabaïn*, $C_{30}H_{46}O_{12}$, which has a physiological action similar to that of strophanthin, but which is twice as toxic, the poisonous dose being about 0·2 mgrm. per kilo. of body-weight (*ibid.* 1888, 765)—Cathelineau, J. Pharm. Chem. 1889, 436; J. Soc. Chem. Ind. 1890, 101. Ouabaïn may be distinguished from strophantin by warming the glucoside with hydrochloric acid and resorcinol. Strophantin gives a rose coloration, whereas ouabaïn gives no coloration, this difference being due to the action of the respective sugars formed by the hydrolysis. Ouabaïn is also obtained from *Strophanthus glaber*, by extracting the seeds, from which the oil has been removed by pressure between filter paper, by shaking with alcohol for several days at a temperature not exceeding 60°. The extract is distilled and the syrupy residue is taken up with water at 50°, filtered, evaporated in a dry vacuum and recrystallised from water (Arnaud, Compt. rend. 1888, 107, 1162).

The crystals obtained by extracting *Strophanthus gratus* (Baill.) with 96 p.c. alcohol also seem identical with ouabaïn (Thoms, Chem. Zentr. 1904, i. 1277).

Ouabaïn forms pearly glistening plates, m.p. 185°–188°, and yields a crystalline hydrate with 9 molecules of water at ordinary temperature, with 4 molecules at 30°, and with 3 molecules at 60°.

The rotatory power of a 1 p.c. aqueous solution of ouabaïn is $[\alpha]_D -30·6°$. Ouabaïn is very sparingly soluble in ether, absolute alcohol, and in chloroform; 100 c.c. of water dissolves 1·57 gram ouabaïn at 30°, 0·93 gram at 14·5°, and 0·66 gram at 8°.

It is readily hydrolysed by dilute acids thus:

$$C_{30}H_{46}O_{12}+H_2O=C_6H_{12}O_5+C_{24}H_{36}O_8$$

forming rhamnose and a red resin which is probably formed by the polymerisation of the second product of hydrolysis (Arnaud, Compt. rend. 1898, 126, 346, 1208). When dried, the resin loses $4H_2O$ and forms $C_{24}H_{28}O_4$. Alkalis do not attack ouabaïn in the cold, but by forming soluble salts they increase its solubility in water and its rotatory power: fused with potash or soda, ouabaïn decomposes at 220°–240° forming oxalic acid, a resin and carbon dioxide (Arnaud, *l.c.* 1280).

With bromine, ouabaïn gives an amorphous derivative containing 60 p.c. of halogen.

Heated with an excess of acetic anhydride at 30°–70°, ouabaïn forms the *heptacetin*, $C_{30}H_{39}O_{12}(C_2H_3O)_7$, m.p. 270°–275° (Arnaud, *l.c.* 349), whilst when ouabaïn is heated with acetic anhydride and zinc chloride at 70° and the cooled product poured into 5–6 times its bulk of water, it forms an *anhydro-heptacetin*, $C_{30}H_{37}O_{11}(C_2H_3O)_7$, m.p. 310° (decomp.), $[\alpha]_D -68·50$ at 85° (in alcoholic solution). On saponification, this acetin yields an acid which is similar to, but not identical with, ouabaïc acid (Arnaud, *l.c.* 1654).

Concentrated nitric acid completely oxidises ouabaïn even in the cold, forming oxalic acid, carbon dioxide and insoluble amorphous nitro derivatives. With more dilute acid (sp.gr. 1·2), no oxalic acid is formed and insoluble crystalline nitro derivatives are produced.

The *di-nitro derivative*, $C_{23}H_{24}(NO_2)_2O_6$, is formed at 40°–75° and crystallises from acetone in yellowish silky needles, m.p. 300° (decomp.). It acts as a dibasic acid and yields crystalline salts. The potassium and sodium salts form orange-red aqueous solutions, the ammonium salt crystallises in golden yellow needles. The *mononitro derivative* $C_{23}H_{25}(NO_2)O_6$ is obtained at 15° or below. It forms yellow anhydrous crystals, m.p. 280° (decomp.), and also yields alkali and ammonium salts. These nitro derivatives are regarded as derived from the compound $C_{24}H_{36}O_8$ which is produced by the hydrolysis of the ouabaïn (Arnaud, *l.c.* 1873).

Ouabaïc acid $C_{30}H_{48}O_{13}$ is obtained by heating a dilute aqueous solution of ouabaïn in a sealed tube at 180°, or better, by heating 1 part of crystalline ouabaïn with 3 parts of strontium hydroxide in 10 parts of water for 12 hours at 100°. The hot solution is saturated with carbon dioxide, filtered, concentrated *in vacuo* and poured, little by little, into 10 times its volume of absolute alcohol. The precipitated strontium salt is dissolved in water and decomposed with sulphuric acid; it is then filtered, and the liquid evaporated *in vacuo*. It is an amorphous, yellow-white substance, m.p. 235° (decomp.), resembling gum in appearance, very soluble in water and in alcohol, but insoluble in ether. It is a dibasic acid which decomposes the alkali and alkaline earth carbonates, forming the corresponding metallic salts. The barium salt $Ba(C_{30}H_{47}O_{13})_2$ has $[\alpha]_D^{20} -46\cdot40°$ in aqueous solution (Arnaud, *l.c.* 1280).

According to Faust (Chem. Zentr. 1902, ii. 1217) *acocantherin*, isolated from *Acocanthera abyssinica* (K. Schum.), is homologous with ouabaïn, being, possibly, the dimethyl derivative. For the physiological and therapeutic action of ouabaïn *v.* Hatcher and Brody, Amer. J. Pharm. 82, 360; Müller, Zeitsch. Allgem. Österr. Apoth. Ver. 1908, 46, 319, 331. *Cf.* STROPHANTHUS.

OUTREMER. ULTRAMARINE (*q.v.*); also PIGMENTS.

OVARIA SICC., OVARINUM, OVARADEN, OVADIN *v.* SYNTHETIC DRUGS.

OXALIC ACID $C_2H_2O_4$, or $\begin{array}{c}COOH\\|\\COOH\end{array}$

This acid occurs as the acid potassium salt in wood-sorrel, garden rhubarb, and many other plants. The spring foliage of many plants such as *Sambucus nigra, Cratægus oxycantha, Æsculus hippocastanum*, contains small quantities of oxalates. Notable quantities of calcium oxalate have been found in *Acacia Cambegii* and other species of *Acacia*. As calcium oxalate, it occurs in many lichens and in certain urinary calculi, and in the free state is found in *Fomes* (*Polyporus*) *igniarius*, in beet leaves, and in the juice of the chick pea. It is one of the constituents of the 'organic non-sugar' in the saccharine products from beet-roots, and to about 2 p.c. in 'saturation mud' of sugar refineries. It is also produced in the oxidation of carbohydrates by a large number of bacilli (Zopf, J. Soc. Chem. Ind. 1900, 386; Banning, *ibid.* 1901, 1151); and also by the action of many fungi and yeasts (Lindner, *ibid.* 1907, 628; Raistrick and Clark, Bio-Chem. J. 1919, 13, 329).

Oxalic acid is occasionally found in beer, due apparently to the action of wild yeasts, and leads to the formation of calcium oxalate crystals in beer deposits (Will, Zeitsch. Ges. Brauw. 1915, 38, 105–116).

It is obtained as an alkaline salt when an alkaline formate is gently heated, and as the ammonium salt when an aqueous solution of cyanogen is kept for some time. The sodium salt is produced by passing carbon dioxide over sodium heated to 360°. The free acid is one of the principal products of the action of nitric acid and other oxidising agents on organic matter.

Preparation.—Moissan has synthesised potassium oxalate by the direct union of carbon dioxide and potassium hydroxide at 80°–200° (Compt. rend. 140, 1209). In the laboratory, oxalic acid may be obtained by gradually adding 8 parts of nitric acid of sp.gr. 1·38 to 1 part of white sugar or starch, heating the mixture to boiling, and evaporating to about one-sixth the original bulk. The crystals obtained on cooling are recrystallised. If stronger acid be used the action is liable to become unmanageable.

This process was formerly employed on the manufacturing scale but has since been superseded by other processes; although possibly the discovery of Naumann, Moeser, and Lindenbaum (D.R. PP. 183022, 208999) that vanadium pentoxide to the extent of 0·001 to 0·002 gram per gram of sugar greatly facilitates the reaction, may give it a new lease of life. By this means, the reaction proceeds at the ordinary temperature, higher yields of oxalic acid are obtained, and no intermediate products result. Before subjecting the carbohydrate to the action of oxides of nitrogen in the presence of vanadium or molybdenum compounds, preliminary treatment of the carbohydrate with the oxides of nitrogen is recommended (Eng. Pats. 14234, 1915; 101680, 1916).

The first process to replace it was the well-known one in which sawdust is heated with caustic alkalis. Starch, straw, bran, and other vegetable matters may be similarly treated, but the best results are obtained with sawdust; fir, pine, poplar, and other soft woods, giving better results than hard woods, such as oak and beech. In order to obtain a finer product, the sawdust is sometimes treated with an alkaline lye to remove resinous and like bodies before fusion.

This process has received many modifications, the chief one being the addition of some oxidising agent. An improvement is patented by Plater-Syberg (Eng. Pat. 23682, 1893). The material rich in carbohydrates, especially wood and moss, is impregnated with caustic alkalis and then heated in presence of an oxidising agent. Hot air, or a mixture of steam and hot air, may conveniently be used as the oxidising agent. Acetates and oxalates are formed, the relative proportion of each depending on the temperature employed. By working at about 120°, acetic acid and a very small quantity of oxalic acid are formed. On raising the temperature to about 300° and increasing the quantity of hot air, the formation of acetic acid almost entirely ceases, whilst oxalic acid is formed in large quantity. Pulp suitable for paper-making is obtained as a by-product. *Cf.* Hedenström (Chem. Zeit. 1911, 35, 853).

A modification of Plater-Syberg's process is that of Zacher (Eng. Pat. 2308, 1897), in which the oxidising material is sodium peroxide or hydrogen peroxide and the heating is carried out in a vacuum. Sawdust or other cellulose material is placed in a steam-jacketed vessel which is exhausted. The contents are then slowly raised to about 70° to deprive the sawdust of moisture and air. Hot alkali lye is then admitted with continued stirring and the vacuum kept constant until a temperature not exceeding 180° is reached. Towards the end of the process, an oxidising agent such as sodium peroxide, hydrogen peroxide, or air enriched with oxygen is admitted. The finished product is dissolved in water in the same vessel, and the solution forced into an open stirring cylinder, in which it is thinned and treated with lime. The calcium oxalate obtained, practically free from carbonate, is decomposed by sulphuric acid. It is stated that a good white oxalic acid is produced by this process with one recrystallisation (*v.* also D. R. P. 103856).

Another method is to oxidise the cellulose-containing materials, in solution of caustic soda or potash of sp.gr. 1·04 to 1·1, with permanganates or manganates. The yields are better than those obtained by heating with caustic potash alone and a much lower temperature is required (Droste, D. R. P. 199583).

Nitrates or chlorates in the presence of Mg salts at a high temperature are also used as oxidising agents (D. R. P. 277733).

Oxalates are also produced together with other products by the process of Cross and Young (Eng. Pat. 28077, 1902). A nitrate or mixture of nitrates is mixed with a carbohydrate of the sugar type, an alkali or alkaline earth, and a little water, and the mass is gradually heated—ultimately to 150°–170°. The main products in this case are cyanide and oxalate. The addition of iron to the mixture produces an excess of cyanide, and the addition of sulphur, or a sulphur compound, a thiocyanate. Ammonia is evolved during the process.

A process for the preparation of oxalic acid and cellulose (Lifschütz, Eng. Pat. 1824, 1891) consists in treating wood, jute, straw, and similar materials with a mixture of dilute nitric and sulphuric acids. The brown vapours evolved, consisting of NO, NO_2 and N_2O_4, are reconverted into nitric acid. The acid liquid is used for other operations, the temperature being gradually increased as the nitric acid becomes exhausted. When this occurs the oxalic acid is crystallised out by cooling. The ligneous material after the action of the nitric acid is converted into cellulose by treatment with a weak alkaline solution.

A completely different method is that of Goldschmidt (Eng. Pat. 26172, 1897). Sodium formate is prepared by the patentee's method of heating sodium carbonate under pressure in a current of carbon monoxide (Eng. Pat. 17066, 1895). 4 parts of crystallised sodium formate are then intimately mixed with 5 parts of anhydrous sodium carbonate and rapidly heated in a molten lead bath at 400°–410°. Air is preferably excluded and the hydrogen evolved is collected. The reaction presumably follows the equation $2HCOONa=(COONa)_2+H_2$. The sodium carbonate is subsequently dissolved out with water at 33°, leaving sodium oxalate.

An improvement on Goldschmidt's method is patented by Wiens who heats formates with previously produced oxalates, in place of sodium carbonate, at 360°–410° (U.S. Pat. 714347, 1902). Koepp and Co. heat the formates with small quantities (less than 5 p.c.) of alkali hydroxide. The mixture rapidly melts, hydrogen is evolved at about 290° and the reaction is complete at 360°, occupying about half an hour in all (Fr. Pat. 331498, 1903; U.S. Pat 748791, 1904; Eng. Pat. 9327, 1903).

Feldkamp (U.S. Pat. 802980, 1905) simplifies the sodium formate method of manufacturing oxalates by heating caustic soda in a current of carbon monoxide and dioxide (water gas or producer gas). The resulting mixture of sodium formate and carbonate is afterwards heated to a higher temperature until the evolution of hydrogen ceases, and a mixture of oxalate and carbonate is produced. The caustic alkali is then regenerated by the addition of slaked lime and precipitated calcium carbonate and oxalate decomposed by sulphuric acid (*v.* also Fr. Pat. 358785, and Eng. Pat. 22225, 1905).

The Electrochemische Werke of Bitterfeld find that oxalates are speedily and evenly produced from formates by heating in a partial vacuum to a temperature below 360°, preferably about 280°. Processes necessitating heating with sodium carbonate or oxalate are improved by working in a vacuum, but the best results are obtained by heating the formate alone (Eng. Pat. 19943, 1907; Fr. Pat. 381245, 1907; D. R. PP. 204895, 269833).

Dugan describes a method by which sodium is sprayed into a pebble mill in which a heated atmosphere of carbon dioxide is maintained (U.S. Pat. 1232249, 1917).

Materials containing cellulose, such as peat, vinasses, sawdust, can be made to yield oxalic acid by treatment with caustic soda or potash in the presence of lime, nitrates, metallic oxides, and air between 170°–190° (Effront, Fr. Pat. 373157, 1906).

Hempel's process consists in heating caustic soda, and carbonate of soda or analogous substances with carbon monoxide under pressure. At 200°–360°, formates are produced, and at higher temperatures up to 420°, oxalates. Oxalates are also produced by heating formates with or without the addition of indifferent substances at 200°–420° under pressure (Fr. Pat. 389039, 1908; Eng. Pats. 3429, 1908; 4897, 1908; 3904, 1908).

The bark of *Shorea rebusta,* which contains considerable quantities of calcium oxalate, has been described as a suitable material for the manufacture of oxalic acid (Eng. Pat. 110837, 1917). The waste liquor from the manufacture of paper pulp is also utilised, oxidation being effected with nitric acid (U.S. Pat. 1217218, 1917).

Bucher describes a process in which sodium cyanide is electrolysed, the cyanogen formed is absorbed by 44 p.c. HCl, whereby it is converted to oxamide and finally by the action of concentrated hydrochloric acid to oxalic acid (J. Ind. Eng. Chem. 1917, 233).

Oxalic acid is usually obtained from the oxalates resulting from these processes by dissolving them in water and precipitating as calcium oxalate, which is filtered off, washed, and decomposed with sulphuric acid. The solution is then filtered, evaporated, and allowed to crystallise. Other methods are used to some extent. McDougall and McDougall obtain oxalic acid by first preparing the potassium salt, adding a suitable sulphate (*e.g.* aluminium sulphate), and sulphuric acid, and separating the resulting alum by crystallisation, adding alcohol if necessary (Eng. Pat. 17971, 1907).

Another method is to add hydrofluoric acid, which precipitates the alum as artificial cryolite, Na_3AlF_6 (G. Müth, D. R. P. 214040). The crude acid is usually somewhat dirty from adherent mother-liquor. It is separated therefrom by a centrifugal cleanser, washed with a minimum quantity of cold water, and recrystallised.

The acid cannot be purified from oxalates by ordinary recrystallisation, but requires to be crystallised from hydrochloric acid of 10 to 15 p.c., which retains the bases as chlorides. A second crystallisation removes the acid. The pure acid may also be prepared by sublimation as described below, or by decomposing the methyl or ethyl ester with water.

For the preparation of pure oxalic acid, Schmatolla recommends crystallisation from absolute alcohol containing a drop or two of sulphuric acid, followed by crystallisation from water, the solution being allowed to stand for several hours in both cases. The crystals are then dried at 30°–40°, and finally over calcium chloride (J. Soc. Chem. Ind. 1901, 496). Riechelmann prefers to crystallise once from ether and once from water (Chem. Soc. Abstr. 1898, i. 239).

Properties.—Oxalic acid crystallises in large transparent monoclinic prisms of sp.gr. 1·641 at 4° (Joule and Playfair), containing two molecules of water.

In an atmosphere dried by sulphuric acid, it gradually loses its water. The water is also gradually evolved and the crystals become opaque when heated at 60° or 70°. As the crystals melt in their water of crystallisation at 98°, and are then somewhat difficult to desiccate, it is advisable to dry the crystals at the lower temperatures. Saturated solutions of oxalic acid lose acid even on the water-bath. The anhydrous acid (dried as above) may be volatilised even at 100° and readily at 157°, and be thus obtained in pure white needles. The temperature should not be allowed to exceed 157°, as considerable decomposition ensues and an inferior product is obtained at 160°.

When oxalic acid is dissolved in 12 parts of warm concentrated sulphuric acid, the solution gradually deposits glistening rhombic pyramids of the anhydrous acid, which rapidly absorb two molecules of water and fall to powder.

Oxalic acid dissolves readily in water and in 2½ parts of cold alcohol. It is also slightly soluble in ether, but is insoluble in chloroform, benzene, and petroleum spirit.

The following table gives the solubility of oxalic acid in water as averaged by Seidell from the results of Alluard; Miezynski (Monatsh. 1886, 7, 258); Henry (Compt. rend. 99, 1157); Lamouroux (*ibid.* 128, 998); and, at 25°, of Foote and Andrew (Amer. Chem. J. 1905, 154):—

	Grms. $(COOH)_2$ per 100 grms.	
t°	H_2O	Solution
0	3·45	3·33
10	5·55	5·26
20	8·78	8·07
25	11·36	10·21
30	13·77	11·91
40	21·15	17·46
50	31·53	23·97
60	45·55	31·37
70	66·82	38·95

Oxalic acid is a powerful reducing agent. The aqueous solution is oxidised at the ordinary temperature in presence of peroxides of lead and manganese. It precipitates gold from solution of the chloride, and, in sunlight, similarly reduces platinum chloride. Oxalic acid reacts with potassium permanganate as follows:

$$2KMnO_4+8H_2C_2O_4 \rightarrow K_2C_2O_4+2MnC_2O_4+10CO_2+8H_2O$$

(J. G. Witt, J. Phys. Chem. 1922, 26, 435). In presence of sulphuric acid it is oxidised by potassium permanganate with production of carbon dioxide and manganese and potassium sulphates. Oxalic acid is not acted on by sulphuric acid at the ordinary temperature, but when heated with the strong acid it is decomposed into carbon monoxide and dioxide without darkening the acid. Phosphoric acid and phosphorus penta- and trichloride also cause the evolution of these gases. Chlorine is without action on the anhydrous acid, but in presence of water it is reduced to hydrochloric acid with evolution of carbon dioxide. Hypochlorites and chlorides of easily reducible metals, such as gold and platinum, have a similar action; bromine water slowly oxidises oxalic acid to carbon dioxide and hydrobromic acid.

A mixture of oxalic acid and crystalline sodium sulphate liquefies in 24 hours giving sodium hydrogen oxalate and sodium hydrogen sulphate (Kohn Abrest, Abs. Chem. Soc. 1917, i. 368).

When exposed to bright light, oxalic acid solutions are decomposed, yielding carbon dioxide and water (Douns and Blunt. Proc. Roy. Soc. 28, 209); by oxidation with nitric acid of sp.gr. 1·4 and upwards, oxalic acid is completely decomposed into these products. According to Richardson (Chem. Soc. Trans. 1894, 452), hydrogen peroxide acts similarly (*cf.* however, Jorissen and Reichler, Chem. Zentr. 1904, i. 81); the reaction is greatly accelerated by certain metals (O. Sulc, *ibid.* 1899, i. 1150). Certain substances have the property of inhibiting the decomposition of oxalic acid solutions. Thymol was first recommended by Gerland (J. Soc. Chem. Ind. 1891, 20), and an examination of a number of substances has been made by Jorissen and Reichler (Chem. Zentr. 1904, i. 359). Oxalic acid is reduced by nascent hydrogen to glycollic acid.

By the action of phosphorus pentachloride (2 mols.), anhydrous oxalic acid (1 mol.), oxalyl chloride $C_2O_2Cl_2$ is formed (*q.v.*).

Solutions of oxalic acid decompose carbonates, phosphates, chromates, &c., and even fluorspar. When heated with sodium or calcium chloride, the powdered acid liberates hydrochloric acid. Potassium and sodium, when heated with the dry acid, cause an evolution of hydrogen with production of a carbonate, the temperature rising to incandescence.

When heated with glycerol between 70° and 90°, oxalic acid is converted into formic acid with evolution of carbon dioxide, glyceryl acid oxalate being formed as an intermediate product (Chattaway, Chem. Soc. Trans. 1914, 151).

The commercial acid and alkaline oxalates frequently contain organic matters which cause charring when heated alone or with sulphuric acid. Sulphates are usually present, and lead and other heavy metals frequently occur. Allen has found as much as 6·3 p.c. of lead oxide in a sample of the acid.

Oxalic acid is largely used as a 'discharge' in calico-printing and dyeing, and for bleaching flax and straw. In dyeing it is used as a substitute for cream of tartar, on account of its cheapness. In the process of 'chroming' wool, its utility lies in its power of forming double salts and in its reducing properties (Körner, J. Soc. Chem. Ind. 1895, 1044). Its property of accelerating the action of chromic acid on indigo is probably due to the formation of a chromium compound of oxalic acid with strong oxidising properties (Prud'homme, *ibid.* 1903, 359, 491; *v.* also Georgevics, *ibid.* 947). The function of oxalic acid in the indigo discharge process has also been studied by Mullerus and Margulies (*ibid.* 1893, 758); Schaposchnikoff and Michireff (*ibid.* 1902, 1276); and Jorissen and Reicher (*ibid.* 1903, 623). Werner (Chem. Soc. Trans. 1904, 1388) finds that by the action of chromic acid on oxalic acid, an acid chromic oxalate, $H_6Cr_2(C_2O_4)_6$, is produced, and his results are confirmed by Jorissen and Reicher (Chem. Zentr. 1904, i. 81). It is also employed for whitening leather, for making formic acid and its esters, and for removing ink or iron stains from fabrics, marble, &c. A solution of Prussian blue in oxalic acid is employed as a blue ink. Oxalic acid forms a constituent of several dyes. Georgevics has prepared a dye-stuff which is yellow in colour, by heating resorcinol with oxalic acid at 160° (J. Soc. Chem. Ind. 1898, 837). Oxalic acid has great cleansing power for brass and other metal, and even for wood-work, and forms a constituent of at least one soap composition for cleaning metals, &c.

Detection and Estimation.—Solutions of calcium salts, even of the sulphate, give precipitates of calcium oxalate, on addition to solutions of oxalates, soluble in mineral acids but not in acetic acid. Free oxalic acid is precipitated by lime water and calcium acetate, but it is better to render the solution alkaline by ammonia and acidify with acetic acid before testing. Pure oxalic acid and oxalates do not char when heated alone or with concentrated sulphuric acid. It decolorises permanganate on warming. Silver nitrate produces with neutral solutions a white crystalline precipitate of silver oxalate which is very explosive when dry.

For estimating this acid, the hot dilute solution, free from mineral acids, or neutralised with ammonia and then acidified with acetic acid, is precipitated with calcium chloride or acetate, or, when sulphates are present, with calcium sulphate. For its estimation in presence of interfering substances, reference must be made to standard works on analysis. After standing for 12 hours, the precipitate is filtered off and dried, and is ignited at a dull, scarcely visible red heat to convert it into carbonate. A little saturated solution of ammonium carbonate is then added to reconvert into carbonate any of the substance which may have become causticised, and the mass is dried and heated sufficiently to remove the whole of the ammonium salt. When the precipitate does not exceed a grain, it is preferably ignited at a bright-red heat over the blow-pipe and weighed as oxide. The ignited precipitate may also be titrated with standard acid.

Another excellent method consists in dissolving the moist precipitate in dilute sulphuric acid and titrating with decinormal permanganate.

This permanganate method is applicable directly to the original substance, provided other oxidisable substances are absent.

Another alternative is to add dilute sulphuric acid to the precipitate in the crucible in sufficient quantity to convert it into calcium sulphate, and subsequently to ignite and weigh as calcium sulphate.

Hydrochloric acid is generally held to interfere with the volumetric estimation of oxalic acid, but according to Baxter and Zanetti (Amer. Chem. J. 1905, 500) oxalic acid may be estimated in the presence of hydrochloric acid with accuracy by titration with permanganate if the initial temperature of titration is not below 70° and the permanganate is run in slowly. The concentration of the hydrochloric acid should not exceed 20 c.c. dilute acid (sp.gr. 1·04) to 150 c.c. oxalic solution, containing not more than 0·3 gram crystallised oxalic acid. Gooch and Peters recommend the addition of a manganese salt (Zeitsch. anorg. Chem. 21, 185). Oxalic acid is occasionally an impurity in hydrogen peroxide in which it may be detected and estimated by nearly neutralising, adding ammonium acetate and subsequently calcium acetate, and treating the calcium oxalate by any of the well-known methods (Roche, J. Soc. Chem. Ind. 1902, 190). Oxalic acid may be estimated in acid beet leaves by the method of Schlösing (Bülow, *ibid.* 1900, 383). The methods of determination in diffusion sugar juice are reviewed by Andrelik and Stanik (*ibid.* 1900, 178).

Heating with resorcinol and dilute sulphuric acid (1 : 1, or even weaker concentration) serves to distinguish oxalic acid from tartaric and lactic acids; the colorations so obtained are: lactic acid, red; lactic acid, green; tartaric acid, yellow (Brauer, Chem. Zeit. 1920, 44, 494; Chernoff, J. Amer. Chem. Soc. 1920, 42, 1784).

Oxalates.

This extensive series of salts includes both normal, acid, and double oxalates, and a class of acid salts known as tetroxalates, apparently produced by the combination of one molecule of oxalic acid with one molecule of an acid oxalate. All oxalates decompose on heating, the alkaline salts forming carbonates. For modes of the decomposition of oxalates on heating, *see* Herschkowitsch, Zeitsch. anorg. Chem. 1921, 115, 159. Only a limited number of oxalates are of technical importance.

Potassium oxalate $C_2O_4K_2,2H_2O$ crystallises in monoclinic prisms or pyramids, readily soluble in water. The *acid salt* C_2O_4HK is found in rhubarb, sorrel, and other plants. It occurs either in anhydrous, monoclinic prisms, or in triclinic crystals containing one molecule of water. The acid salt, which is much less soluble than the normal salt, forms with oxalic acid *potassium tetroxalate* $C_2O_4KH{\cdot}C_2O_4H_2,2H_2O$, which forms triclinic crystals soluble in 20 parts of water at 20°.

Both these acid salts are sold as 'salts of sorrel' or 'salts of lemon,' and are used for removing ink stains, &c., and also for scouring metals, cleansing wood, &c., for which they are at least as suitable as the free acid.

The normal salt may be prepared by neutralising the acid with potash or potassium carbonate. The acid salt may be made by halving a solution of the acid, neutralising one part, and adding the other. The tetroxalate is similarly prepared by neutralising one-fourth of the solution and adding the remainder, or by adding 75 parts of potassium chloride to 252 parts of oxalic acid, both in saturated solution. Potassium oxalate is employed in the hot bath used in the platinotype process, and is also used in other photographic operations.

Solutions of potassium hydrogen oxalate

tend to break up into the normal potassium oxalate and the tetroxalate. The latter salt may be crystallised from a not too concentrated solution of the acid salt at 10°.

Sodium oxalate $C_2O_4Na_2$ occurs in various plants growing in salt marshes. It and the acid salt are prepared similarly to the potassium compounds. No quadroxalate has yet been prepared. The normal salt requires about 36 parts of cold water for solution. It separates from hot solutions in fine glistening needles or as a crystalline powder. The acid salt is still less soluble.

Ammonium oxalate $C_2O_4(NH_4)_2 2H_2O$ occurs in Peruvian guano. It crystallises in long rhombic prisms readily soluble in water. The acid salt is less soluble, crystallises in rhombic prisms and gives a tetroxalate isomorphous with that of potassium. These salts are prepared similarly to the potassium salts.

Ammonium tetroxalate is occasionally found as a crystalline deposit, of m.p. 130°, in samples of commercial amyl nitrite formed by its decomposition (Sandgrist and Mohlin, Ber. 1920, 58, 171).

Calcium oxalate C_2O_4Ca is widely distributed in the vegetable kingdom and is the least soluble of the calcium salts. It occurs in rhubarb and other plants, frequently in aggregations of needle-like crystals. In larger proportions it occurs in many lichens which grow on limestone, and in certain urinary calculi. It is precipitated as a powder containing one molecule of water, by addition of a calcium salt to an oxalate. When heated to 180° it becomes anhydrous, but it reabsorbs water when exposed to the air. The acid salt has not been prepared.

Barium and *strontium oxalates* resemble the calcium salts, but are somewhat soluble in water. The neutral *magnesium oxalate*, and double oxalates of magnesium with potassium and ammonium but not with sodium, are known. The acid magnesium oxalate has not been prepared.

Cuprous oxalate is prepared by sprinkling cuprous sulphite into a hot solution of oxalic acid. It is obtained as a brown substance combined with $2H_2O$. On heating it changes to a grey colour, loses water, and finally undergoes violent decomposition (Daniels, J. Amer. Chem. Soc. 1915, 1167).

Ferrous oxalate occurs in lignite combined with $1\frac{1}{2}H_2O$ as *humboldtine*. It may be prepared as a heavy yellow, nearly tasteless powder, almost insoluble in cold, and sparingly soluble in hot water, by mixing ferrous sulphate with oxalic acid or an oxalate; or in fine lemon-coloured crystals by exposure of a solution of hydrous ferric oxide in oxalic acid. It is also slowly deposited from a solution of iron in oxalic acid. The artificial variety contains $2H_2O$. An acid oxalate appears to exist.

Ferrous oxalate is employed as a developer in photography. The solution used is obtained by adding ferrous sulphate solution to excess of potassium oxalate. The ferrous oxalate exists in the resulting brown solution as a double ferrous potassium oxalate $K_2Fe(C_2O_4)_2,2H_2O$. When heated it is converted into a mixture of iron and finely divided oxide, admirable as a rouge for optical purposes.

Ferric oxalate. The normal salt is slowly deposited as a yellow precipitate on mixing a normal oxalate with ferric chloride, or on treating freshly precipitated ferric hydroxide with a quantity of oxalic acid insufficient to dissolve the whole. The solution in oxalic acid gradually deposits ferrous oxalate on exposure to the light. Double salts with the alkalis are obtained by dissolving ferric hydroxide in acid alkaline oxalates. These are used in photography in the preparation of platinum printing papers. Sodio-ferric oxalate

$$Na_3Fe(C_2O_4)_3,4\frac{1}{2}H_2O$$

forms large green crystals. The ferric ammonium oxalate is sometimes used instead of the double citrate for producing blue prints in photography.

Antimony oxalates. The application of antimony oxalate and the double oxalates with the alkaline metals in calico-printing has been noted under article ANTIMONY, Vol. I. The normal salt $Sb_2O_3{\cdot}C_4O_6,2H_2O$ is obtainable by boiling antimonious chloride or oxychloride in oxalic acid, or by mixing a saturated solution of oxalic acid with a hydrochloric acid solution of the trichloride. It crystallises out as a granular precipitate. The antimony potassium oxalate $SbK_3(C_2O_4)_3,6H_2O$ is obtained in monoclinic crystals from a solution of antimonic acid in acid potassium oxalate. It is used as a mordant in dyeing. The sodium salt $SbNa_4(C_2O_4)_4,10H_2O$ is similarly prepared.

Cerium oxalate $Ce_2(C_2O_4)_3,10H_2O$ is a white, slightly granular, insoluble powder, permanent in the air, odourless and tasteless. It may be prepared by the action of oxalic acid solution on cerous oxide, or by addition of oxalic acid to a soluble cerium salt. Cerium oxalate has medicinal properties resembling those of bismuth subnitrate, and is used to prevent the vomiting of pregnancy and in certain diseases (Jolin, Bull. Soc. chim. [ii.] 21, 540).

Methyl oxalate $C_2O_4(CH_3)_2$ is obtained in rhombic tables melting at 54° and boiling at 163° by dissolving anhydrous oxalic acid in methyl alcohol and washing the crystals with cold water. Methyl oxalate is converted into oxalic acid and methyl alcohol by boiling with water. Pure oxalic acid may thus be prepared (*v.* METHYL).

Ethyl oxalate $C_2O_4(C_2H_5)_2$ is a liquid which may be obtained by slowly heating a mixture of 3 parts of the anhydrous acid and 2 parts of absolute alcohol to 100°, afterwards heating to 125° or 130° while the vapour of 2 parts of absolute alcohol is passed in. The ethyl oxalate is separated by fractional distillation. This compound is an aromatic oily liquid boiling at 186° and is decomposed by water in the same manner as methyl oxalate. Treated with phosphoric chloride at 150°–155° it yields a mixture of ethyl chloride, phosphoryl chloride, and *oxalyl chloride* $C_2O_2Cl_2$ (Fauconnier, Compt. rend. 114, 122).

A great number of aromatic esters of oxalic acid have been prepared and characterised by Bischoff and Hedenström (Ber. 1902, 3437); and also by Anselmino (Ber. Deutsch Pharm. Ges. 1903, 494).

The decomposition of oxalates on heating, though taking place approximately according to the equation $CaC_2O_4 = CaCO_3 + CO$ in the case of calcium oxalate is in reality more complex.

Some carbon is always produced during the ignition of calcium oxalate. Sodium and barium oxalates follow the courses

$$7Na_2C_2O_4 = 7Na_2CO_3 + 3CO + 2CO_2 + 2C$$

and $8BaC_2O_4 = 8BaCO_3 + 6CO + CO_2 + C$

Magnesium oxalate gives equal volumes of CO and CO_2 and no carbon, $MgC_2O_4 = MgO + CO + CO_2$; but most other oxalates give notable quantities of carbon dioxide and carbon (Scott, Chem. Soc. Proc. 1904, 156).

The electrolytic reduction of oxalic acid and oxalates in sulphuric acid solution to derivatives of glyoxylic acid was first patented by Portheim (U.S. Pat. 798920, 1905).

Kinzlberger and Co. (D. R. P. 163842) reduce oxalic acid, its esters, and amide electrolytically in a cell with a lead cathode and a diaphragm in presence of sulphuric acid of strengths varying from 2 to 90 p.c. monohydrate. The current density is 2 to 10 amps. per sq. cm. and the temperature must be kept low. Oxanilic acid or its derivatives in the same conditions yield phenylglycine or a derivative (*v.* also U.S. Pat. 837083; D. R. PP. 204787, 194038). Kinzlberger & Co. have since secured an additional patent for the use of electrodes of metals not attacked by sulphuric acid, particularly mercury (D. R. P. 210693). Bayer & Co. make use of sodium amalgam in the reduction of oxalic acid derivatives (D. R. P. 201895; J. Soc. Chem. Ind. 1908, 1176).

OXALIC ACID FERMENTATION *v.* FERMENTATION.

OXALYL BROMIDE $C_2O_2Br_2$, formed by the action of phosphorus pentabromide upon anhydrous oxalic acid, or better, by treating oxalyl chloride with hydrogen bromide. A greenish-yellow liquid, b.p. 102°–103°/720 mm., m.p. −19·5°. Is readily decomposed by heat into carbon monoxide, bromine, and carbonyl bromide, and is more reactive than the corresponding chloride (Staudinger and Anthes, Ber. 1913, 46, 1426).

OXALYL CHLORIDE $C_2O_2Cl_2$ was first obtained by Fauconnier (Compt. rend. 1892, 114, 122) by heating diethyl oxalate (1 mol.) with phosphoric chloride (2 mols.), but is more easily prepared by the action of phosphorus pentachloride (2 mols.) on anhydrous oxalic acid (1 mol.). It forms white crystals, m.p. −12°, b.p. 64°/763 mm., reacts quantitatively with water, yielding carbon dioxide, carbon monoxide, and hydrogen chloride, and is converted into oxalic acid when treated in the gaseous state with water vapour, into oxalates by alcohols, and into oxamides by amines. Forms carbonyl chloride and carbon monoxide when heated to 600°, or when boiled with aluminium chloride in carbon disulphide solution, and may therefore be employed in place of carbonyl chloride in the Friedel-Crafts synthesis (Staudinger, Ber. 1912, 45, 1594).

With ethyl mercaptan oxalyl chloride in cold ethereal solution forms *ethyl dithio-oxalate* $C_2O_2(SEt)_2$, a viscid, yellow oil, b.p. 238°–240°/757 mm., m.p. 24°–25° (m.p. 27°–27·5°, b.p. 235°, Jones and Tasker, Chem. Soc. Trans. 1909, 1904), light yellow crystals (Staudinger, Ber. 1908, 41, 3558).

For the action of oxalyl chloride on amines and amides, *see* Bornwater, Proc. K. Akad. Wetensch, Amsterdam, 1911, 14, 42; Chem. Soc. Abstr. 1911, i, 161.

For its action on aromatic hydrocarbons, *see* Liebermann, Ber. 1912, 45, 1186; on polynuclear hydrocarbons, Liebermann and Kardos, Ber. 1913, 46, 198. It affords a satisfactory means of introducing carboxyl groups into aromatic hydrocarbons, and when methyl groups are also present in the phenyl radicle, higher carboxylic acids are readily obtained on oxidation. Oxalyl chloride differs in its action from phosgene, which mainly yields ketones, and probably acts in virtue of the complex CO·COCl. For the action of oxalyl chloride on carbonyl compounds, *see* Staudinger, Ber. 1909, 42, 3966; Chem. Soc. Abstr. 1909, i. 905. On dimethylaniline, *see* Staudinger and Stockmann, Ber. 1909, 42, 3485; Chem. Soc. Abstr. 1909, i. 796.

Methyl dithio-oxalate $(CO{\cdot}S{\cdot}CH_3)_2$, pale yellow crystals, m.p. 82·5°–83·5°.

Propyl dithio-oxalate $(CO{\cdot}S{\cdot}C_3H_7)_2$, yellow liquid, b.p. 158°/15 mm.

iso-*Amyl dithio-oxalate* $(CO{\cdot}S{\cdot}C_5H_{11})_2$, yellow liquid, b.p. 206°/19 mm.

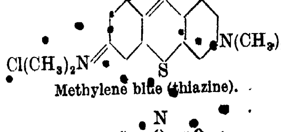
Phenyl dithio-oxalate $(C_{14}H_{10}O_2S_2)$, sulphur yellow prismatic needles, m.p. 119°–120°, readily soluble in ether or light petroleum.

By the action of alcoholic potassium hydrosulphide on these substances also in alcoholic solution, the alkyl mercaptan is formed and *potassium dithio-oxalate* $C_2O_2S_2K_2$ results. Very soluble in water; forms large colourless prisms. Unstable. Solution gives yellow or orange-yellow precipitates with metallic salts, which decompose on heating (Jones and Tasker, *l.c.*).

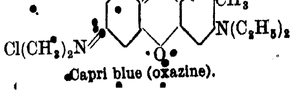
For other reactions with oxalyl chloride, *see* Franchimont, Proc. K. Akad. Wetensch. Amsterdam, 1913, 16, 376; Folpmers, Rec. trav. chim. 1915, 34, 34; Figee, *ibid.* 1915, 34, 289; Liebermann, Kardos and Mühle, Ber. 1915, 48, 1648: Bornwater, Rec. trav. chim. 1915, 35, 124; 1917, 36, 250; Adams and Weeks, J. Amer. Chem. Soc. 1916, 38, 2514; Adams, Wirth and French, *ibid.* 1918, 40, 424; Gina, Gazz. chim. ital. 1917, 47, i. 51; Copisarow, Chem. Soc. Trans. 1918, 113, 819.

OXAMINE BLUE, -MAROON, -RED, -VIOLET *v.* AZO- COLOURING MATTERS.

OXAZINE COLOURING MATTERS.—The colouring matters of this series are closely related in structure to those of the thiazine group, the only difference in their general formulæ being caused by the replacement of the coupling sulphur atom by oxygen. Two typical examples in Capri blue and methylene blue will illustrate this statement:

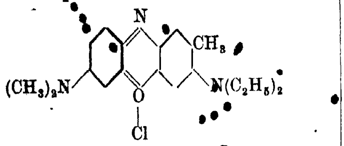


Methylene blue (thiazine).



Capri blue (oxazine).

Constitution.—The formula for Capri blue given above represents this substance as a derivative of *p*-quinone-diimide in which salt formation is produced on the imido nitrogen as in, for example, magenta. Within recent years, attempts have been made to assign to the oxazines an ortho-quinone formula of the same character as that which is now generally accepted as best expressing the structure of the colouring matters of the azine series. On this basis the formula of Capri blue becomes



in which salt formation is represented as having taken place through the passage of diad into tetrad oxygen. The work of Kehrmann and others shows that many of the properties of these compounds can be better explained by the oxonium formula than by the para-quinone structure. In the present article the oxonium formulæ have been used mainly for the sake of uniformity, although it must be remembered that it is by no means certain that the para-quinone structure of the salt is incorrect.

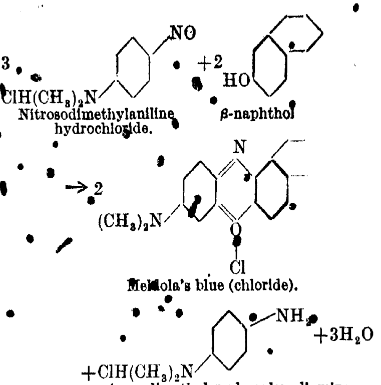
General description and methods of preparation.—The colouring matters of the series may be conveniently classed under two heads: (*a*) the basic colours; (*b*) the mordant colours.

(*a*) *The basic colours.*—These compounds are the hydrochlorides, sulphates, and, in some cases, the zinc chloride double salts of the oxazine bases. The most typical member is **Meldola's blue**, which was prepared by Meldola in 1879 and was the first colour of the series to be isolated. In the first instance the preparation was effected by allowing *β*-naphthol to react with nitrosodimethylaniline hydrochloride in glacial acetic acid solution. At the present time alcohol is used as a solvent and the colour is obtained by the following means.

Manufacture.—A mixture of 20 kilos. of *β*-naphthol, 20 kilos. of nitrosodimethylaniline hydrochloride, and 90 kilos. of alcohol is gradually heated in an enamelled pan fitted with a reflux condenser, set in a water-bath, until a vigorous reaction sets in. The solution is quickly run out of the pan and is isolated as the zinc chloride double salt by adding a solution of zinc chloride until no further precipitate is obtained. The crystals which separate are centrifuged, washed with about 35 kilos. of alcohol and dried. The yield is 28 kilos. (Schultz, Farbstofftabellen, 5th ed. 221).

Properties.—The colour is a dark violet powder, soluble in water forming a bluish-violet solution. It dyes cotton mordanted with tannic acid and tartar emetic an indigo shade of blue.

Mechanism of formation.—There is no doubt that the formation of an oxazine colouring matter, in the manner described above, involves the reduction of one-third of the nitrosodimethylaniline used to *asym*-dimethyl-*p*-phenylenediamine and that the equation representing the formation of Meldola's blue can be written as follows:—



Nitrosodimethylaniline hydrochloride. *β*-naphthol

Meldola's blue (chloride).

Asym-dimethyl-*p*-phenylenediamine.

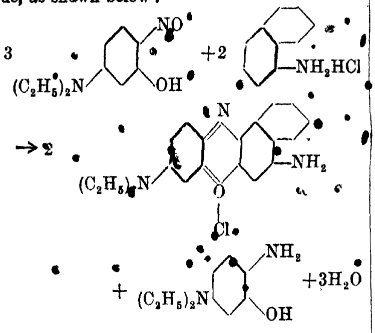
Literature.—Meldola (Ber. 1879, 12, 2065; Chem. Soc. Trans. 1881, 39, 37); Nietzki and Otto (Ber. 1888, 21, 1745); Witt (*ibid.* 1890, 23, 2247); Nietzki and Bossi (*ibid.* 1892, 25, 2294). Meldola's blue appears in commerce under other names of which the following are the more important: new blue R, fast blue, cotton blue, fast navy blue, and naphthol blue..

It is evident from the above equation that the formation of an oxazine colouring matter of the type of Meldola's blue might be expected to ensue when any derivative of *β*-naphthol is treated with a derivative of nitrosodimethylaniline provided that in the one case the adjacent position to the hydroxyl group is unoccupied and in the other the ortho-position to the nitroso-group is free. In practice, however, the formation of colours of this character is confined to the simpler reaction. Nevertheless, a new method for the preparation of these colours was introduced by Reissig in 1888, and by its means a number of important colours were added to the group. The new process can be best illustrated by referring to the production of **Nile blue A**, which is produced by the interaction of nitrosodiethyl-*m*-aminophenol hydrochloride and *α*-naphthylamine.

Preparation.—A quarter litre flask, fitted with an air condenser, containing 10 grams of *α*-naphthylamine hydrochloride dissolved in 100 grams of glacial acetic acid and 20 grams of water, is heated on the sand-bath until the contents are at the boiling-point when 17 grams of nitrosodiethyl-*m*-aminophenol hydrochloride are added in small portions at a time. The vigorous reaction which is caused by each addition is allowed to subside before a fresh portion is added. When all the phenol has been used the mixture is allowed to boil for half an hour when the colouring matter separates as glistening crystals on cooling.

Properties.—Crystalline powder, with marked bronze reflex, soluble in water, alcohol or pyridine forming a blue solution. Dissolves in concentrated sulphuric acid forming an orange-red solution which, on dilution, passes through green to blue. It is employed for the dyeing of tannined cotton on which it produces a bright shade of blue.

Mechanism of formation.—The formation of Nile blue A may be expressed by an equation similar to that given in the case of Meldola's blue, as shown below:

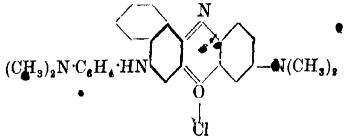


Literature.—Reissig (B. A. S. F.), Eng. Pats. 4476, 1888; 11046, 1891; U.S. Pat. 431541; D. R. PP. 45268; 74391; Fr. Pat. 189358; Bayer, D. R.-P. 49844; Fr. Pat. 198588; Möhlau and Ullmann (Annalen, 289, 111); Thorpe (Chem. Soc. Trans. 1907, 91, 324). The commercial product in usually the sulphate.

Other members of class (*a*) may be summarised as under; they are employed as tannin cotton colours.

Capri blue is formed from nitrosodimethylaniline and diethyl-*m*-aminocresol (Bender, 1890), and the **Cresyl blues** (Bender, 1892) are derived from nitrosodialkyl-*m*-amino-*p*-cresol and meta- or para-diamines.

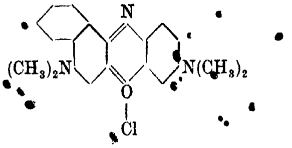
New blue B is formed by the condensation of *asym*-dimethyl-*p*-phenylenediamine with Meldola's blue:



It has been already stated that this base is a by-product in the formation of Meldola's blue. It therefore follows that New blue is always present in small quantities in commercial Meldola's blue.

In its manufacture a mixture of 21 kilos. of β-naphthol, 30 kilos. of nitrosodimethylaniline hydrochloride, and 90 kilos. of alcohol are heated to about 70° for about 2 hours and the colouring matter is precipitated by the addition of an alcoholic solution of 6·6 kilos. of zinc chloride.

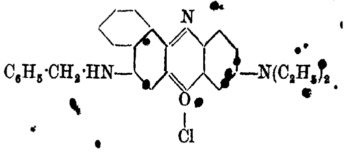
New methylene blue is formed by the action of dimethylamine on Meldola's blue:



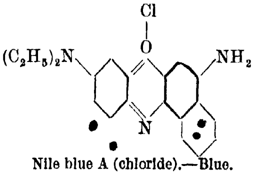
It dyes cotton mordanted with tannin a greenish-blue, fast to light and washing and is also employed for the dyeing of silk.

New fast blue F, H (New Indigo blue F, R).—These dyes are obtained by condensing tetra-alkyldiaminobenzhydrols with Meldola's blue. They dye tannin-mordanted cotton in various shades of indigo blue.

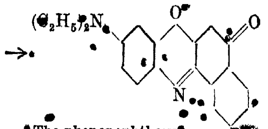
Nile blue 2B is formed by the condensation of nitrosodiethyl-*m*-aminophenol hydrochloride and benzyl-α-naphthylamine (P. Julius, 1891):



The basic colours of this series have been used for some considerable time as stains for the purpose of colouring microscope sections; like other basic colours, they stain the nitrogenous parts of the section leaving the neutral regions uncoloured. It has been shown by Lorrain Smith (J. Path. Bact. 1907, 12, 1) that certain colours of the oxazine series possess the curious property of staining sections containing nitrogenous matter and neutral fat differentially; that is to say, whilst the nitrogenous matter is coloured blue in the usual manner the neutral fat is stained red. The colouring matter which exhibits this property to the greatest degree is Nile blue A, and there is no doubt that the cause of this behaviour is due to the partial hydrolysis of the dye in solution, thus:



Nile blue A (chloride).—Blue.



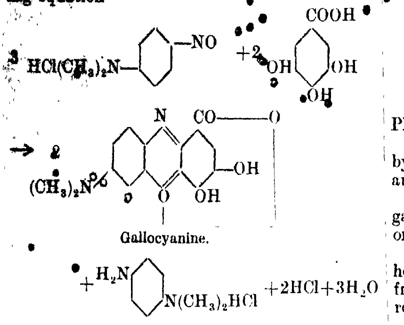
The phenonaphthoxazone.—Red.

It is found (Chem. Soc. Trans. 1907, 91, 324) that small quantities of the oxazine are formed so soon as the dye is dissolved in water and that it is readily extracted by neutral solvents. It is evident, therefore, that the staining of the neutral fat is due to the extraction of the oxazine by the fat.

(*b*) *The mordant colours.*—The colouring matters of this section are prepared by the condensation of nitrosodialkylanilines with compounds of the type of gallic acid. The oxazine contains, therefore, two hydroxyl groups in the ortho- position to the coupling oxygen atom; consequently, like alizarin, they yield insoluble lakes with metallic salts and can be employed as mordant colours. A typical member of this group is **Gallocyanine**, which can be prepared by the condensation of nitrosodimethylaniline with gallic acid.

Manufacture.—A mixture of 75 kilos. of gallic acid, 35 kilos. of nitrosodimethylaniline hydrochloride, and 850 litres of methyl alcohol is boiled under a reflux condenser, 80 kilos. of nitrosodimethylaniline hydrochloride are added gradually during 3 to 4 hours, and the whole is heated until all the nitrosodimethylaniline hydrochloride has disappeared. On cooling, the product is filtered off, washed with 700 litres of water, and dried. The colouring matter is a bronze powder insoluble in water. It dyes chrome-mordanted wool bluish-violet, and is also used for printing upon chrome-mordanted wool and cotton.

Mechanism of formation.—The course of the reaction, which is of the same character as that already shown, can be illustrated by the following equation—



Literature.—H. Köchlin, D. R. P. 19580, 1881; Eng. Pat. 4899, 1881; Fr. Pat. 145685; U.S. Pats. 253721, 257498; Mon. Scien. 1883 (3) 13, 292; Nietzki and Otto (Ber. 1888, 21, 1736; 1892, 25, 2994).

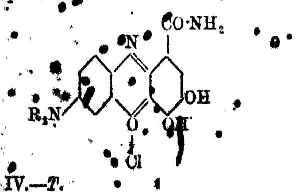
The other dyestuffs of this group are, for the most part, derived either directly from gallocyanine by the action of various reagents, or by processes in which gallic acid or a derivative of this substance is employed. The following are the more important members.

Delphine blue (Hagenbuch, 1889) is prepared by sulphonating the product formed by heating gallocyanine hydrochloride with aniline. When the interaction is carried out in the cold an isomeric colouring matter, **Chromazurine**, is obtained. The **Chromocyanines** (de la Harpe and Vaucher, 1898) are formed by the action of sulphites on gallocyanines.

Indalizarin (de la Harpe and Vaucher, 1900) is obtained from the gallocyanine sulphonic acids by the action of sulphites.

Gallamine blue (Geigy, 1889) is formed by the action of nitrosodimethylaniline on gallamide.

Coreine 2R (**Cœlestine Blue B**) (Bierer, 1893) is the corresponding diethyl derivative. It is probable that the formulæ of these compounds is best expressed by the structure:

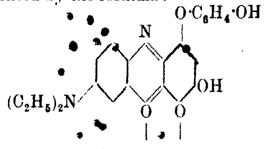


Coreine AR is derived from Coreine 2R by the action of aniline and subsequent sulphonation.

Ultracyanine B is produced by condensing gallocyanine with resorcinol; its reduction product is known as **Ultracyanine R.**

The **Phenocyanines** (de la Harpe, 1893) are obtained by the action of resorcinol on the gallocyanine which is formed by the condensation of nitrosodiethylaniline and gallic acid.

Phenocyanine VS is the initial product, and **Phenocyanine TC** is formed from this by the oxidising action of air; its structure is probably represented by the formula:

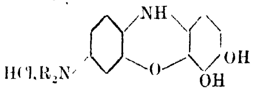


Phenocyanine TV is the sulphonic acid of Phenocyanine TC.

Gallanilic violets (Möhler, 1889) are formed by the action of nitrosodialkylanilines on the anilide of gallic acid.

Modern violet (**Blue 1900 TC**) is a leucogallocyanine obtained by reducing gallocyanine or its derivatives.

Modern violet N (**Gallo violet**) is obtained by heating the gallo- and leuco-cyanines, derived from gallic acid, to 100°. The constitution is represented by the formula:



An analogous colouring matter is **Chromo heliotrope** (**Modern heliotrope**), obtained by the action of nitrosomonoalkylarylamines on gallic acid or its derivatives with subsequent reduction.

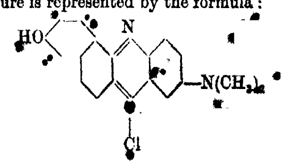
Modern Cyanine (**Anthracyanine, Chromacetine**), produced by the interaction of gallocyanine and aromatic diamines, dyes chrome-mordanted cotton greenish-blue. It is used chiefly in calico-printing.

Modern blue (**Gallo green DH**) is obtained by treating gallocyanine with formaldehyde. It is used for obtaining green to dark blue shades in calico-printing.

Prune pure, prepared from nitrosodimethylaniline hydrochloride and methyl gallate, is also much used in calico-printing for obtaining bluish-violet shades.

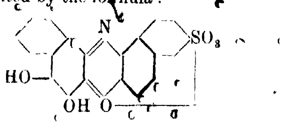
The above colours are largely used for the dyeing of chrome-mordanted wool on which they produce various shades of blue and violet. The colouring matters given below also belong to the oxazine series:—

Muscarine (Annaheim, 1885) is prepared by the action of nitrosodimethylaniline hydrochloride on 2·7-dihydroxynaphthalene. Its structure is represented by the formula:

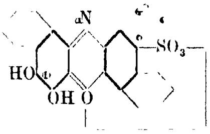


It is employed in the dyeing of tannined cotton on which it produces a fairly fast shade of blue.

The **Alizarin Greens** (Elsässer, 1895) are prepared from β-naphthoquinone sulphonic acid and certain aminonaphtholsulphonic acids. Thus **Alizarin Green G** is produced when β-naphthoquinone sulphonic acid is condensed with 1-amino-2-naphthol-6-sulphonic acid and is represented by the formula :

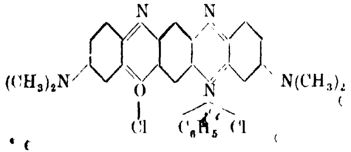


Alizarin Green B is formed from the corresponding 2-amino-1-naphthol-4-sulphonic acid and has the structure :



Both colouring matters produce fast shades of green on chrome-mordanted fabrics.

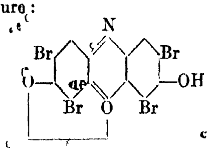
Fast Black (Bender, 1889) is formed by the condensation of nitrosodimethylaniline with *m*-hydroxydiphenylamine. The structure of this compound is, in all probability, represented by the formula :



The dyestuff produces an extremely fast shade of blue-black on tannin-mordanted cotton.

Resorcin Blue (Ullrich, 1898) is always produced directly on the cotton fibre by treating the material, impregnated with tannic acid and resorcin, with nitrosodimethylaniline.

Fluorescent Blue (**Iris Blue**) (Weselsky and Benedict, 1880) is made by the bromination of resorufin, a compound which is produced by heating nitrosoresorcinol with resorcinol in the presence of concentrated sulphuric acid. It has the structure :



and dyes silk and wool a fairly bright shade of blue, the dyed fabric retaining, to a certain extent, the brownish fluorescence of the dye solution.

J. F. T.

OX-GALL *v.* Bile.

OXIDISED OILS *v.* Oils (Fixed) and Fats.

OXINDOLE *v.* Amino-acids (aromatic).

OXONITE *v.* Explosives.

OXONITINE *v.* Aconitine.

OXOZONE *v.* Ozone.

OXYACANTHINE $C_{19}H_{19}NO_3$. An alkaloid associated with berberine and berbamine in berberis root (Hesse, Ber. 19, 3190).

OXYANTHRARUFIN. *Oxychrysazin v.* Alizarin and allied colouring matters.

OXYAZO- DYES *v.* Azo- dyes.

OXYCAMPHOR *v.* Synthetic drugs.

OXYCANNOBIN *v.* Resins.

OXYDASES. The term 'oxydase' was first applied by Bertrand to the group of oxidising ferments which possess certain characteristics common to enzymes. Although there is much in the behaviour of the oxydases which distinguishes them sharply from other enzymes, particularly the fact that they are generally associated with manganese, it is customary to regard them as enzymes and to define them as substances which, under physiological conditions, rapidly carry oxygen to materials on which otherwise oxygen would act very slowly.

Oxydases act as catalysts, their activity rises to an optimum with increase of temperature and then falls with a further rise: it is destroyed on boiling. They are insoluble in alcohol, absorbed by colloidal precipitates and unable to dialyse. Although it is claimed that the more recent researches point definitely away from this hypothesis, they are selective in their action, different oxydases acting only on certain groups of more or less closely related materials.

The power of effecting oxidation is accompanied by a marked absorption of oxygen from the surrounding atmosphere.

Oxydases are so universally distributed and take part in so many natural phenomena, particularly those which are manifested externally by colour changes, that it is surprising so little is understood as yet about the mechanism of their action. A number of reagents have been employed in their study: few of these are really satisfactory.

The most extensively used are guaiacum, which gives a blue coloration and precipitate; quinol, which is oxidised to quinone (Bertrand, Compt. rend. 1894, 18, 1215); pyrogallol, which gives insoluble purpurogallin (Bach and Chodat, Ber. 1904, 37, 1342); vanillin, which forms insoluble dehydrovanillin (Herzog and Meier, Zeitsch. physiol. Chem. 1908, 57, 35; 1909, 59, 57). The behaviour of tyrosinase is studied on tyrosine which becomes first red, then black and finally gives a black precipitate. Salicylic aldehyde, the leucobase of malachite green, phenolphthalein, &c., have also found employment. [For a complete list of oxydase reagents and references to the original papers, *v.* Kastle, U.S. Treasury Dept. Hygienic Laboratory, Bulletin No. [illegible]]

One of the most satisfactory reagents is benzidine as used by Keeble and Armstrong (Proc. Roy. Soc. 1913, 87B, 125) both for general work and for the localisation of oxydases *in situ* in plant issues. This is used either in ½ p.c. solution in 50 p.c. ethylalcohol or as a saturated solution in 1 or 2 p.c. sodium chloride. Blue or violet · brown colorations or precipitates are obtained when the reaction is positive, owing to the formation of meri-quinonoid salts of diphenoquinonediimine with benzidine itself. In the paper cited the colour reactions with oxydase given by various phenols either alone or in admixture are discussed at length.

The better known oxydases are—

1. *Laccase*, which oxidises guaiacum, quinol, tannin, &c., and is very widely distributed in plants.

2. *Tyrosinase*, which oxidises tyrosin and allied substances: it occurs in both plants and animals. Less studied have been—

3. *Aldehydase*, an animal oxydase, which oxidises salicylaldehyde and other aromatic aldehydes.

4. *Indophenol oxydase*, which is widely distributed in animal tissues: it forms indophenol from α-naphthol and *p*-phenylenediamine (Röhmann and Spitzer, Ber. 1895, 28, 567). In addition, enzymes known as *peroxydases*, which oxidise reagents only in presence of a peroxide like hydrogen peroxide, are universally distributed in living cells and tissues.

The view is gaining ground that oxydases are not entities but in reality mixtures of a peroxydase and an unstable organic peroxide (Moore and Whitley, Biochem. J. 190[illegible], 4, 136; Bach and Chodat, Ber. 1903, 36, 606). Many plants contain organic bodies capable of autoxidation, thereby becoming organic peroxides. This superoxidation may be caused by an enzyme—the *oxygenase*. These two components, peroxide and peroxydase, are essential to the constitution of an oxydase.

Catalases are ferments which decompose hydrogen peroxide but cannot effect the oxidation of oxydase reagents, a distinction first drawn by Loew (Bulletin No. 66, U.S. Dept. Agric. 1901). They are very widely distributed in vegetable and animal tissues. Catalase is soluble in water and destroyed by heat. Considerable interest attaches to the catalase (hemase) of blood (Senter, Zeitsch. physikal. Chem. 1903, 44, 257; 1905, 51, 673).

It has been suggested that the function of catalase is to protect the organism against excessive oxidation, but the inability to decompose substituted organic peroxides or oxygenases (Bach and Chodat, Ber. 1903, 36, 1756) and other facts are against this view and the question is as yet but imperfectly understood.

Peroxydases and catalases are so widely distributed in living tissues that their presence might almost be used as a chemical test for vital activity. They are characterised by great stability: thus the peroxydase of horse-radish is not entirely destroyed when its solution is boiled for a short time. The activity of a weak oxydase is greatly increased by a peroxydase, more especially by that from the same source as itself. They gradually lose their activity during the oxidations which they bring about.

Peroxydases appear invariably to contain manganese, and Bertrand (Compt. rend. 1897, 124, 1032, 1355) has shown that the oxidising power of laccase is proportional to the amount of manganese present; further, that the addition of a small amount of manganese greatly increased the oxidising power of lucerne laccase. He therefore regards manganese as the co-ferment of laccase in the same way as hydrochloric acid is the co-ferment of pepsin. The manganese cannot be replaced by other metals in the case of laccase, but iron and other metals have similar functions with other enzymes. Colloidal suspensions and solutions of these metals have been shown to form artificial peroxydase systems. The subject is a complex one. For literature, *see* Kastle, *l.c.*

Tyrosinase. An oxidising ferment acting on tyrosine is widely distributed in both plants and animals. When the enzyme is added to a solution of tyrosine, the mixture becomes red, then black and deposits finally a black precipitate. The amount of action is conveniently measured by titrating with 0·002 normal potassium permanganate after the addition of sulphuric acid (Bach, Ber. 1908, 41, 216) until the colour of the titer disappears.

This change is responsible for the reddening and subsequent blackening observed in certain fungi and in the roots and tubers of plants. Tyrosinase is also of importance in the formation of animal pigments—melanins as they are termed (*v.* von Fürth and Schneider, Beitr. chem. Physiol. Path. 1901, 1, 229; also von Fürth and Jerusalem, *ibid.* 1907, 10, 131).

Tyrosinase is entirely different from laccase which usually accompanies it in plants. The peroxydase of laccase activates hydrogen peroxide towards guaiacum, quinol, pyrogallol, &c., but not towards tyrosine, whilst the peroxydase of tyrosinase acts only on tyrosine and certain amino compounds and does not affect the laccase reagents.

Vegetable tyrosinase is best obtained from fungi—species of *Russula* or *Agaricus*—or from wheat bran (Bertrand and Mutermilch, Compt. rend. 1907, 144, 1385). The young fresh fungus is macerated with chloroform water or with glycerol, or the enzyme may be precipitated from the aqueous extract by alcohol (Bach, Ber. 1908, 41, 221). 300 c.c. of clear expressed fungus juice is poured into 1·5 litres of 96 p.c. alcohol: the precipitate is filtered, washed with alcohol and dried in a vacuum. The activity depends on the age of the fungus.

To obtain it from wheat bran, 1 part is allowed to stand with 4 parts water—the mixture is centrifuged and the solution mixed with 3 vols. of 95 p.c. alcohol. The precipitate is separated, washed and dissolved in distilled water. The enzyme is again precipitated by alcohol, collected and dried *in vacuo*: the substance obtained amounts to 0·8 p.c. and contains no laccase.

Sources of animal tyrosinase are the ink sac of the cuttle fish and the pupæ of the butterfly of the species *Deiciphilia euphorbiæ* (von Fürth and Jerusalem, *l.c.*).

Tyrosinase is sensitive to the action of acids and alkalis and certain poisons, particularly hydrocyanic acid. It obeys the laws of mass action in the production of melanin from tyrosine (Bach, Ber. 1908, 41, 221).

Tyrosinase acts equally well on racemic, dextro- and lævo- tyrosine. It gives characteristic colours with compounds analogous to tyrosine containing a phenolic hydroxyl (Bertrand, Bull. Soc. chim. 1908, [iv.] 3, 335). It gives colour changes with homogentisic acid and tryptophane and with polypeptides containing tyrosine; the latter are not coloured like tyrosine but become yellow, then orange and finally mahogany red. The nature of the amino acid modifies the colour (Abderhalden and Guggenheim, Zeitsch. physiol. Chem. 1907, 54, 331; also Chodat and Staub, Arch. Sci. Phys. Nat. 1907, 23, 2[illegible]5; 1907, 24, 172).

[illegible] in the presence of an amino compound, particularly an amino acid, a series of coloured substances is produced the colours of which depend on the nature of the amino compound. Subsequently (Arch. Sci. Phys. Nat. 1913, 35, 140) he has shown that carbon dioxide, formaldehyde and ammonia are produced, when a vegetable oxydase acts on glycine or other amino acid. *See* further Keeble, Armstrong and Jones, Proc. Roy. Soc. 1913, 87B, 113, for the bearing of these results on the formation of anthocyan pigments.

Laccase is of almost universal distribution in the vegetable kingdom, but its occurrence in animals is rare. It is soluble in water and active aqueous extracts are readily obtained from most plant materials, the potato and cabbage being convenient sources. It is more stable towards heat and alcohol than tyrosinase, the latter being destroyed at 70°: laccase is killed on boiling. Most acids and substances, such as hydrogen cyanide and hydrogen sulphide, destroy its activity.

It may be salted out from solution by ammonium sulphate. It is not specific in its action but promotes the oxidation of a large number of easily oxidisable substances. It is responsible for the colour changes occurring in cut fruit like apples, pears, &c., the brown colour formed being considered to be due to the oxidation of tannin by laccase (Lindet, Compt. rend. 1895, 120, 370; Kastle and Loevenhart, Amer. Chem. J. 1904, 31, 606).

The problems of industry in which oxydases play a part are very numerous and great developments await their successful solution. Such questions as the prevention of the browning of fruits and vegetables during drying are of the utmost importance if full use is to be made of such articles of food which are relatively perishable in the fresh state: oxydases play a large part in these changes. The presence of an oxydase probably accounts for the fact that the perfumes of many flowers rapidly deteriorate after picking, especially if they are bruised. Again, the formation of aldehydes and ketones in essential oils is perhaps largely due to the action of such enzymes (*cf.* Brooks, J. Amer. Chem. Soc. 1912, 34, 67).

In the case of the sugar beet Bunzel (Biochem. Zeitsch. 1913, 50, 185) has shown that any general abnormal disturbances of growth lead to an increased oxydase content of the leaves. A study of the distribution of the oxydase in the expressed juices of this plant showed that [illegible] of the presence [illegible].

A very complete [illegible] summary and bibliography of the literature bearing on oxydases is given by J. H. Kastle, Bulletin 59, Hygienic Laboratory, [illegible] 1910.

The most recent work of [illegible] and Hopkins (Proc. Roy. Soc. [illegible]) affords valuable proof that a [illegible] of oxydases is an enzymic catalyst in the [illegible] sense of the word. They show that milk, like certain animal tissues, contains a catalyst which in the presence of methylene blue, is able to bring about the oxidation of both xanthin and hypoxanthin to uric acid under strictly anaerobic conditions. The oxydase is highly specific as no other purine derivative tested could induce the reduction of methylene blue. It is remarkable that, when the bases are in equimolecular concentration, hypoxanthin reduces twice as fast as xanthin and therefore uric acid is produced at equal velocity in each case, the former base taking up two atoms of oxygen as fast as the latter takes up one atom. It is further of interest that under aerobic conditions hypoxanthin takes twice as long as xanthin for complete conversion into uric acid. The authors consider that the same catalytic system is responsible for both anaerobic oxidation and that in presence of oxygen. It is not difficult to understand, for example, that once some association between the catalyst and the hydrogen and oxygen acceptors is established, the two atoms of oxygen required by hypoxanthin may be as readily available as the one required by xanthin since the concentration of water which is the source of oxygen is indefinitely large. Under aerobic conditions, the velocity of change depends on the rate of supply of air (oxygen), which is relatively slow. The fact that the enzyme can influence two centres simultaneously is of considerable interest.

E. F. A.

OXYDISILIN Si_2H_2O. A white solid substance formed by treating calcium silicide with cold dilute hydrochloric acid in the dark. Has powerful reducing properties and is spontaneously inflammable in air. Treated with bromine forms *silical bromide* Si_2OHBr, hydrolysed by water to *silical hydroxide*, a strong base of a red colour, forming salts with hydrochloric, sulphuric, acetic, and formic acids, of a yellow colour, and decomposed by water. Oxydisilin with carbon tetrachloride yields silical chloride and phosgene. The silical compounds are oxidised by alkalis to silica with evolution of hydrogen (Kautsky, Zeitsch. anorg. Chem. 1921, 117, 209).

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END OF THE FOURTH VOLUME.

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